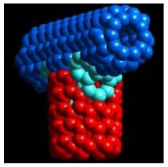
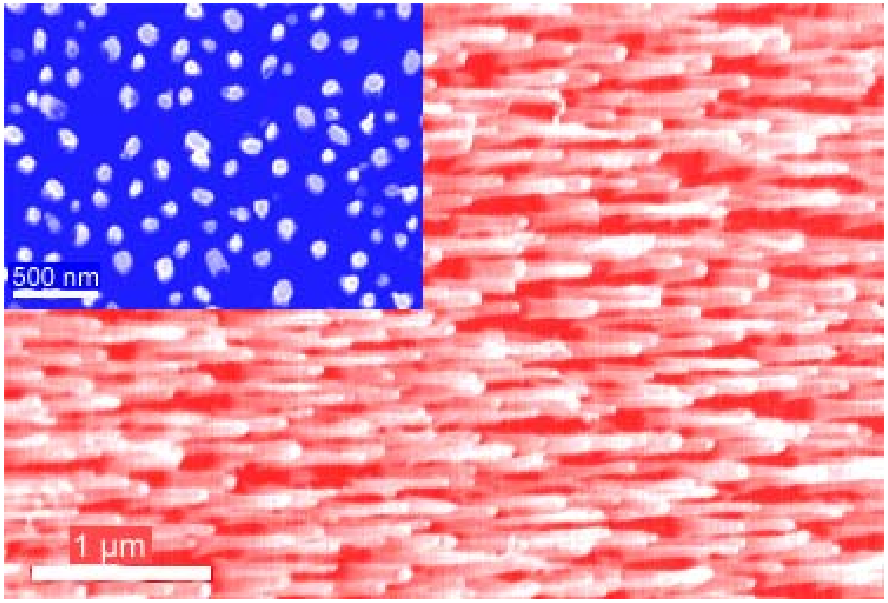
Carbon Nanotube Based Nanotechnology





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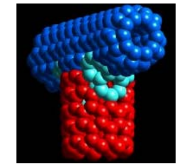

Agenda

- Nanotechnology and NASA
- Carbon Nanotubes
    - CNT - growth and characterization
    - CNT based microscopy
    - CNT based biosensors
- Some other Nano examples

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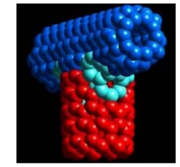
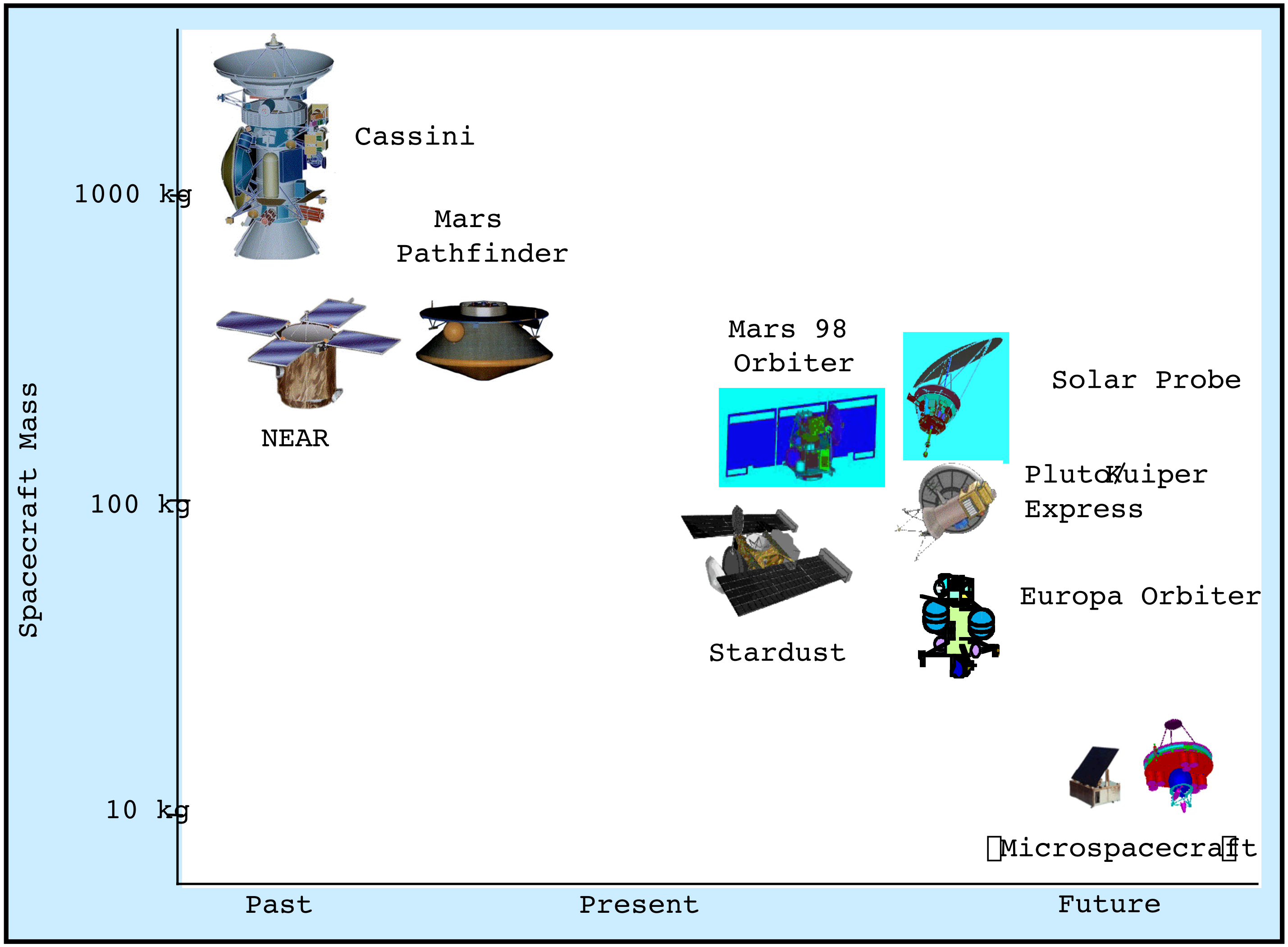
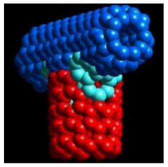
NASA's Own Moore's Law





Why Nanotechnology at NASA?



- Advanced miniaturization, a key thrust area to enable new science and exploration missions
  - Ultrasmall sensors, power sources, communication, navigation, and propulsion systems with very low mass, volume and power consumption are needed

- Revolutions in electronics and computing will allow reconfigurable, autonomous, “thinking” spacecraft

- Nanotechnology presents a whole new spectrum of opportunities to build device components and systems for entirely new space architectures
  - Networks of ultrasmall probes on planetary surfaces
  - Micro-rovers that drive, hop, fly, and burrow
  - Collection of microspacecraft making a variety of measurements

Europa Submarine

Just one Material, so much Potential

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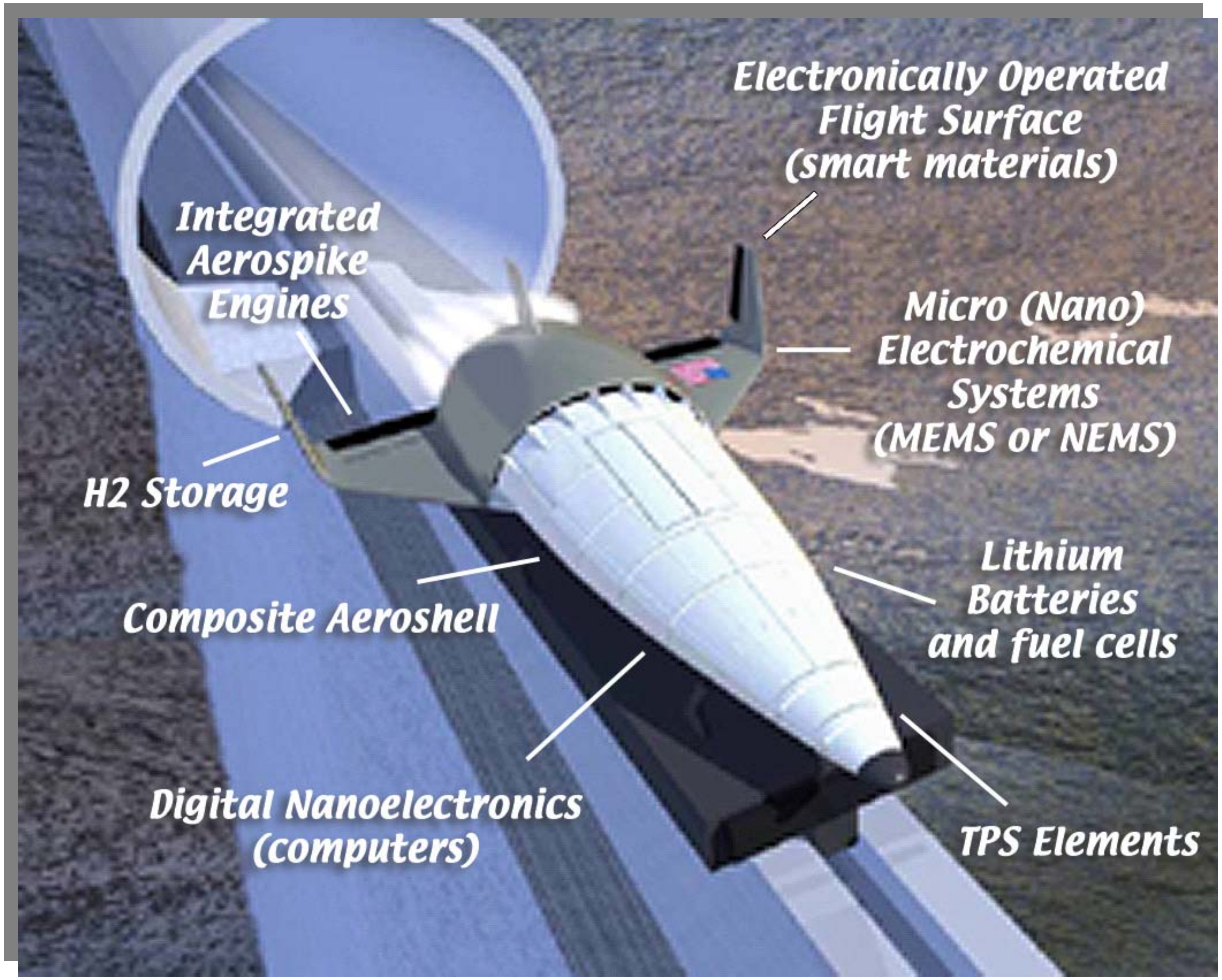

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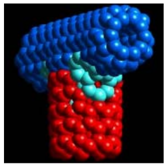
NASA's Investments in Nano



- NASA Ames Center for Nanotechnology, started in 1996, is the largest in-house R & D in Federal Government; consists of 50 scientists and engineers working on various aspects of experimental and computational nanotechnology fields.

- NASA Ames has strong collaboration with the academia
  - undergraduate student research program
  - high school student research program

- Smaller programs at JSC (CNT composites), Langley (Nano materials), Glenn (Energy storage), and JPL

- NASA's university-based Nano-Institutes
  - Three institutes, \$3 M/year/institute for 5 + optional 3 years (Purdue, UCLA, Princeton/Texas A & M)

- Recent spin-off: Integrated Nanosystems, Inc.

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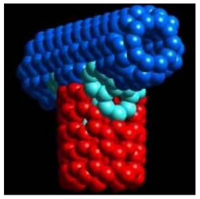
NASA Ames Nanotechnology Research Focus



* Carbon Nanotubes
- Growth (CVD, PECVD)
- Characterization
- AFM tips
  - Metrology
  - Imaging of Mars Analog
  - Imaging Bio samples
- Electrode development
- Biosensor (cancer diagnostics)
- Chemical sensor
- Logic Circuits
- Chemical functionalization
- Gas Absorption
- Device Fabrication

* Molecular Electronics
- Synthesis of organic molecules
- Characterization
- Device fabrication

* Inorganic Nanowires

* Protein Nanotubes
- Synthesis
- Purification
- Application Development

* Genomics
- Nanopores in gene sequencing
- Genechips development

* Computational Nanotechnology
- CNT - Mechanical, thermal properties
- CNT - Electronic properties
- CNT based devices: physics, design
- CNT based composites, BN nanotubes
- CNT based sensors
- DNA transport
- Transport in nanopores
- Nanowires: transport, thermoelectric effect
- Transport: molecular electronics
- Protein nanotube chemistry

* Quantum Computing

* Computational Quantum Electronics
- Noneq. Green’s Function based Device Simulator

* Computational Optoelectronics

* Computational Process Modeling

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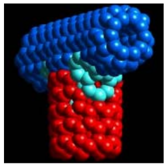
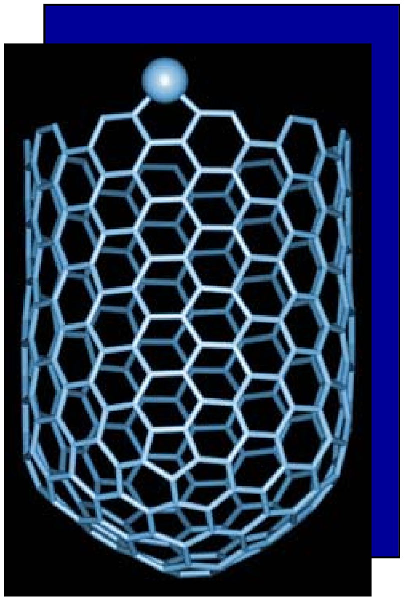
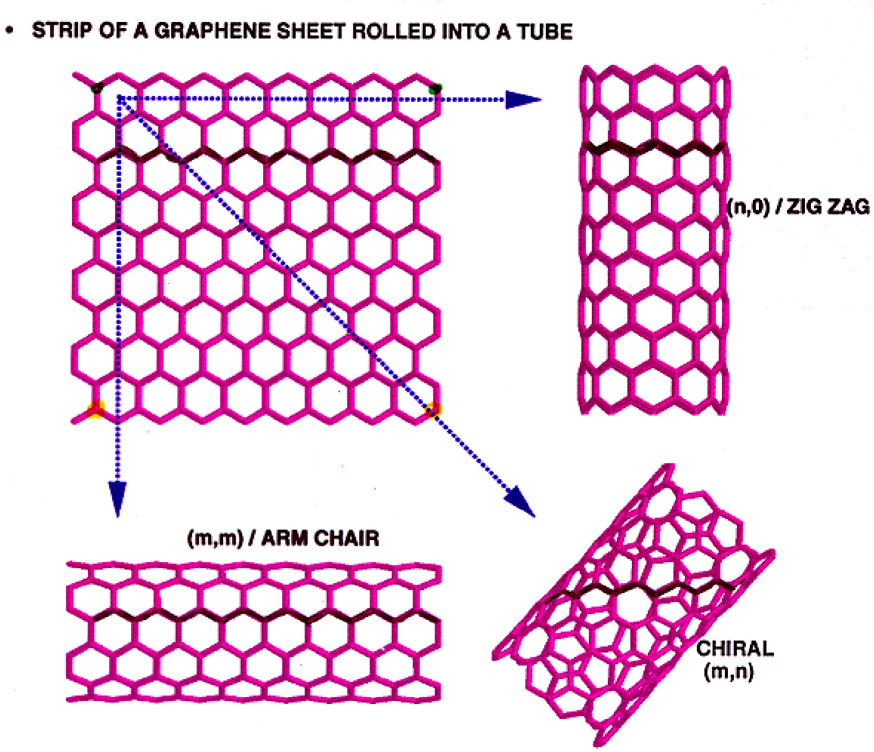
Carbon Nanotube





CNT is a tubular form of carbon with diameter as small as 1 nm.
Length: few nm to microns.

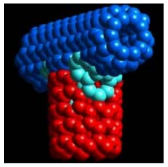
CNT is configurationally equivalent to a two dimensional graphene sheet rolled into a tube.

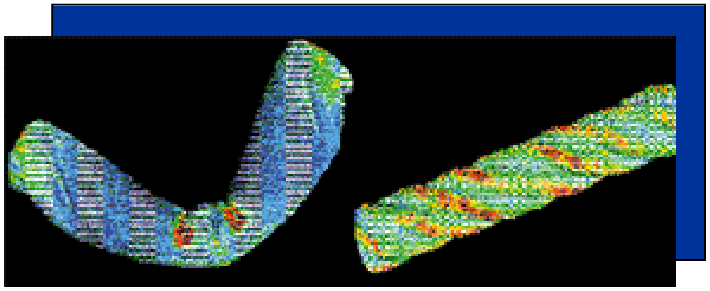


CNT exhibits extraordinary mechanical properties: Young's modulus over 1 Tera Pascal, as stiff as diamond, and tensile strength ~ 200 GPa.

CNT can be metallic or semiconducting, depending on chirality.

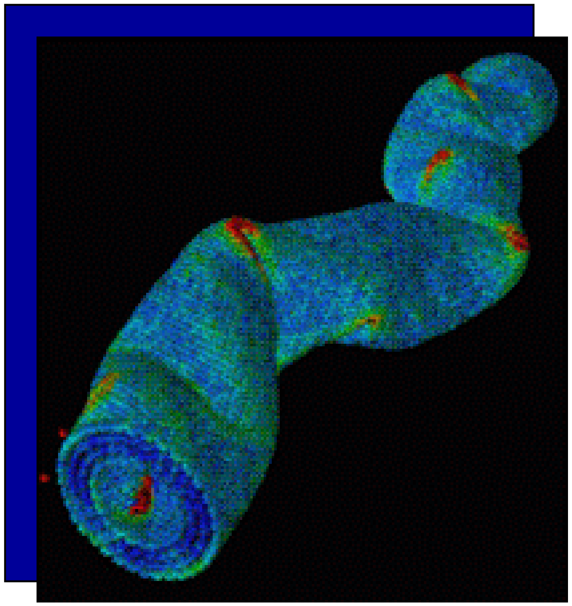
CNT Properties





- The strongest and most flexible molecular material because of C-C covalent bonding and seamless hexagonal network architecture

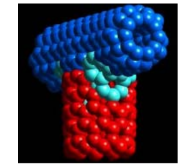
- Young's modulus of over 1 TPa vs 70 GPa for Aluminum, 700 GPA for C-fiber
    - strength to weight ratio 500 time > for Al; similar improvements over steel and titanium; one order of magnitude improvement over graphite/epoxy



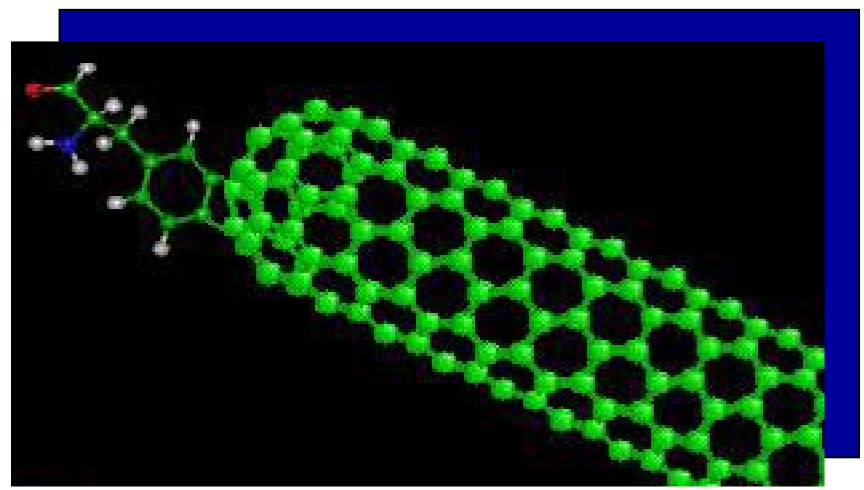
- Maximum strain ~10% much higher than any material

- Thermal conductivity ~ 3000 W/mK in the axial direction with small values in the radial direction

CNT Properties (cont.)



- Electrical conductivity six orders of magnitude higher than copper
- Can be metallic or semiconducting depending on chirality
  - ‘tunable’ bandgap
  - electronic properties can be tailored through application of external magnetic field, application of mechanical deformation…
- Very high current carrying capacity
- Excellent field emitter; high aspect ratio and small tip radius of curvature are ideal for field emission
- Can be functionalized



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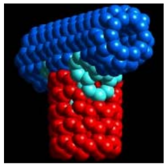
CNT Applications: Structural, Mechanical

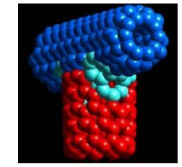


- High strength composites
- Cables, tethers, beams
- Multifunctional materials
- Functionalize and use as polymer back bone
  - plastics with enhanced properties like "blow molded steel"
- Heat exchangers, radiators, thermal barriers, cryotanks
- Radiation shielding
- Filter membranes, supports
- Body armor, space suits

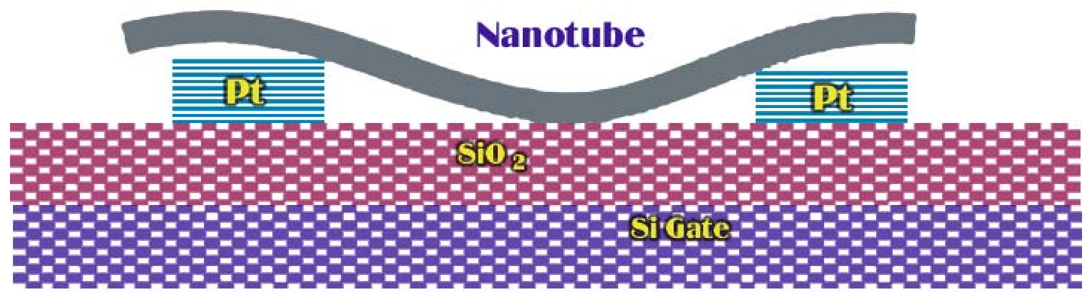
Challenges

- Control of properties, characterization
- Dispersion of CNT homogeneously in host materials
- Large scale production
- Application development

CNT Applications: Electronics



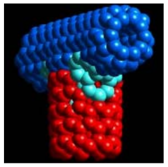
- CNT quantum wire interconnects
- Diodes and transistors for computing
- Capacitors
- Data Storage
- Field emitters for instrumentation
- Flat panel displays
- THz oscillators



Challenges

- Control of diameter, chirality
- Doping, contacts
- Novel architectures (not CMOS based!)
- Development of inexpensive manufacturing processes

CNT Applications: Sensors, NEMS, Bio



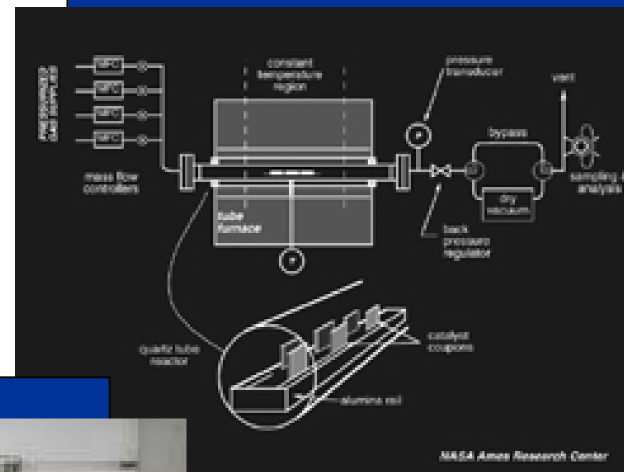
- CNT based microscopy: AFM, STM…
- Nanotube sensors: force, pressure, chemical…
- Biosensors
- Molecular gears, motors, actuators
- Batteries, Fuel Cells: H_2, Li storage
- Nanoscale reactors, ion channels
- Biomedical
  - in vivo real time crew health monitoring
  - Lab on a chip
  - Drug delivery
  - DNA sequencing
  - Artificial muscles, bone replacement, bionic eye, ear...

Challenges

- Controlled growth
- Functionalization with probe molecules, robustness
- Integration, signal processing
- Fabrication techniques

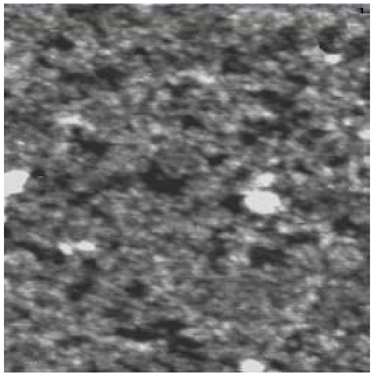
CNT Synthesis

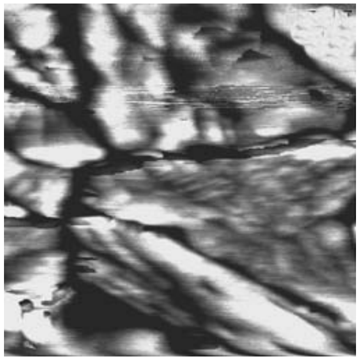
- CNT has been grown by laser ablation (pioneering at Rice) and carbon arc process (NEC, Japan) - early 90s.
  - SWNT, high purity, purification methods
- CVD is ideal for patterned growth (electronics, sensor applications)
  - Well known technique from microelectronics
  - Hydrocarbon feedstock
  - Growth needs catalyst (transition metal)
  - Multiwall tubes at 500-800° deg. C.
  - Numerous parameters influence CNT growth



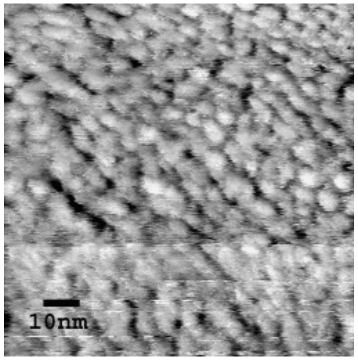
Catalyst Characterization

- Catalyst surface characterized by AFM (with SWNT tip) and STM.
- AFM image of as-sputtered 10 nm iron catalyst (area shown is 150 nm x 150 nm). Also, the same surface after heating to 750° C (and cooled) showing Fe particles rearranging into clusters.





- STM image of a nickel catalyst showing nanoscale particles



- These results are consistent with high resolution TEM showing particles as small as 2 nm.

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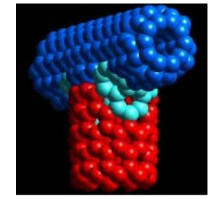
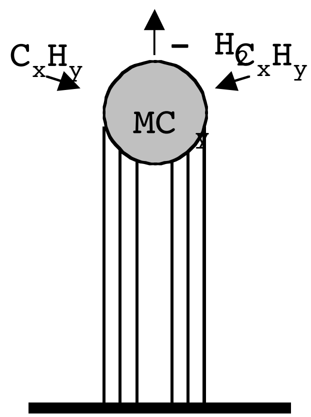
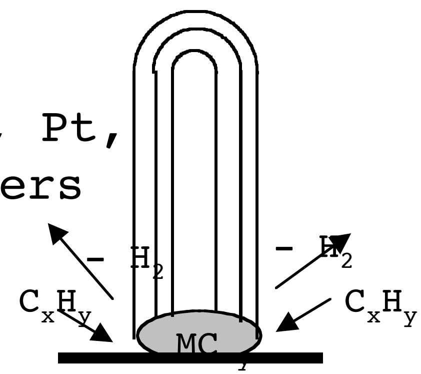
CVD Growth Mechanisms For Carbon Nanotubes



- Adsorption and decomposition of feedstock on the surface of the catalyst particle
- Diffusion of carbon atoms into the particle from the supersaturated surface
- Carbon precipitates into a crystalline tubular form
- Particle remains on the surface and nanotube continues to lengthen - “base growth” mechanism
- Growth stops when graphitic overcoat occurs on the growth front - “catalytic poisoning”



M = Fe, Ni, Co, Pt, Rh, Pd and others



Tip Growth

Typically occurs when there are very weak metal-surface interactions

Base Growth

Occurs when the metal-surface interactions are strong

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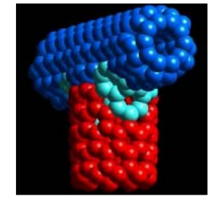
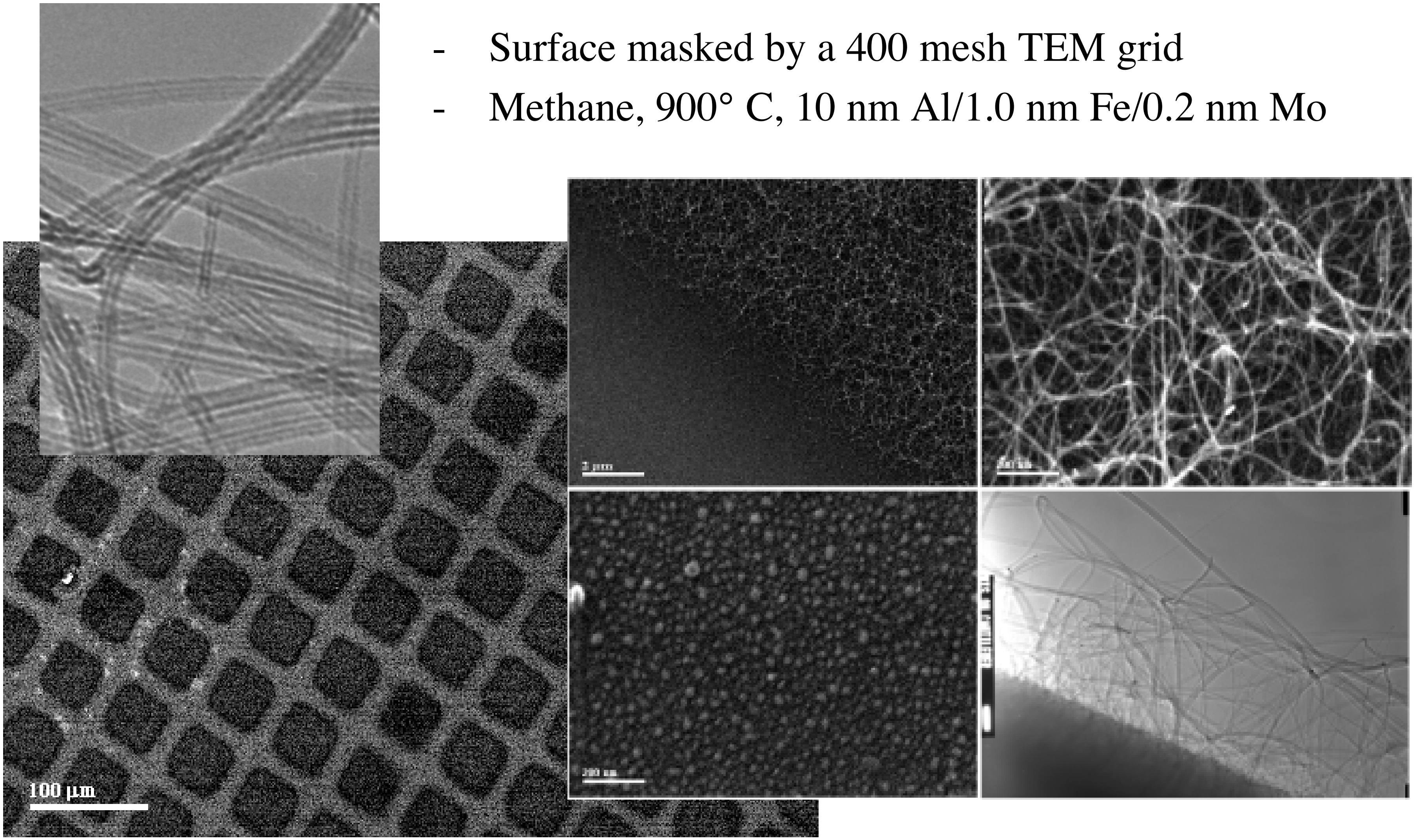
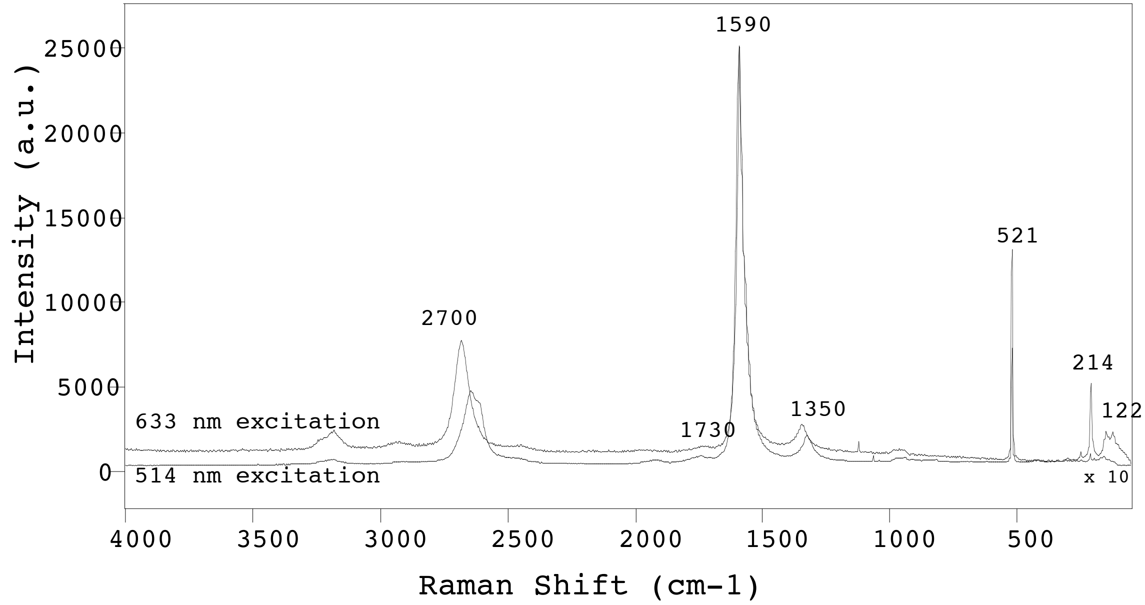
SWNTs on Patterned Substrates



- Surface masked by a 400 mesh TEM grid
- Methane, 900° C, 10 nm Al/1.0 nm Fe/0.2 nm Mo

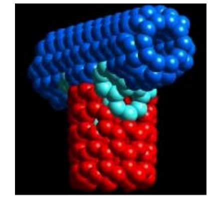


Raman Analysis of SWNTs

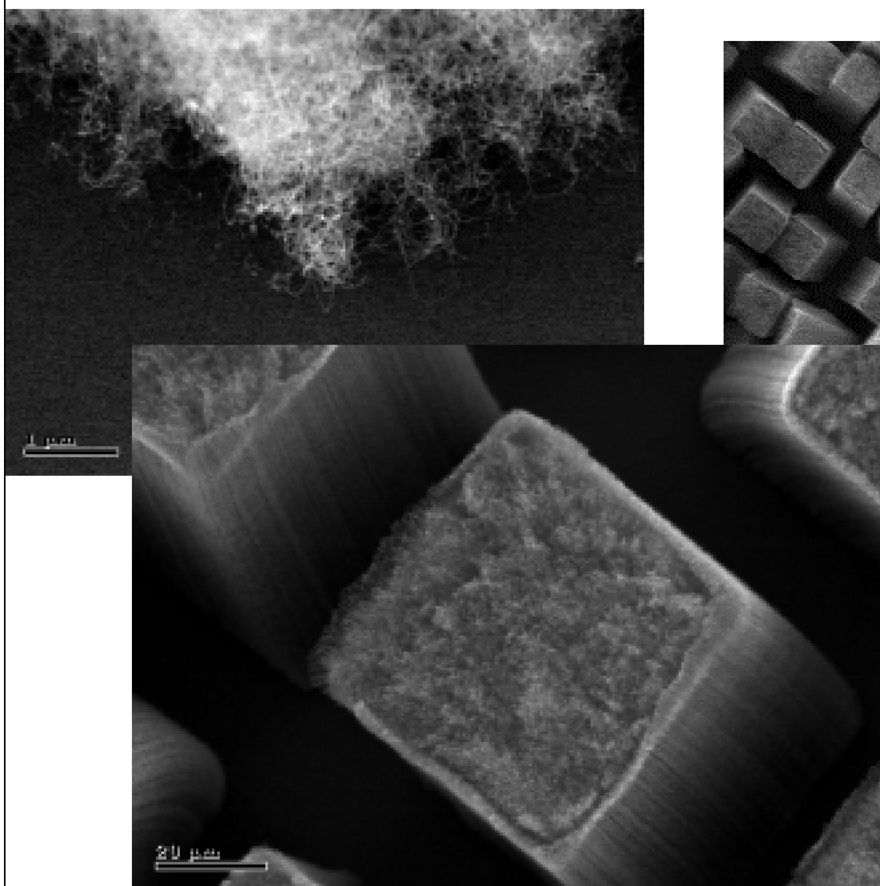


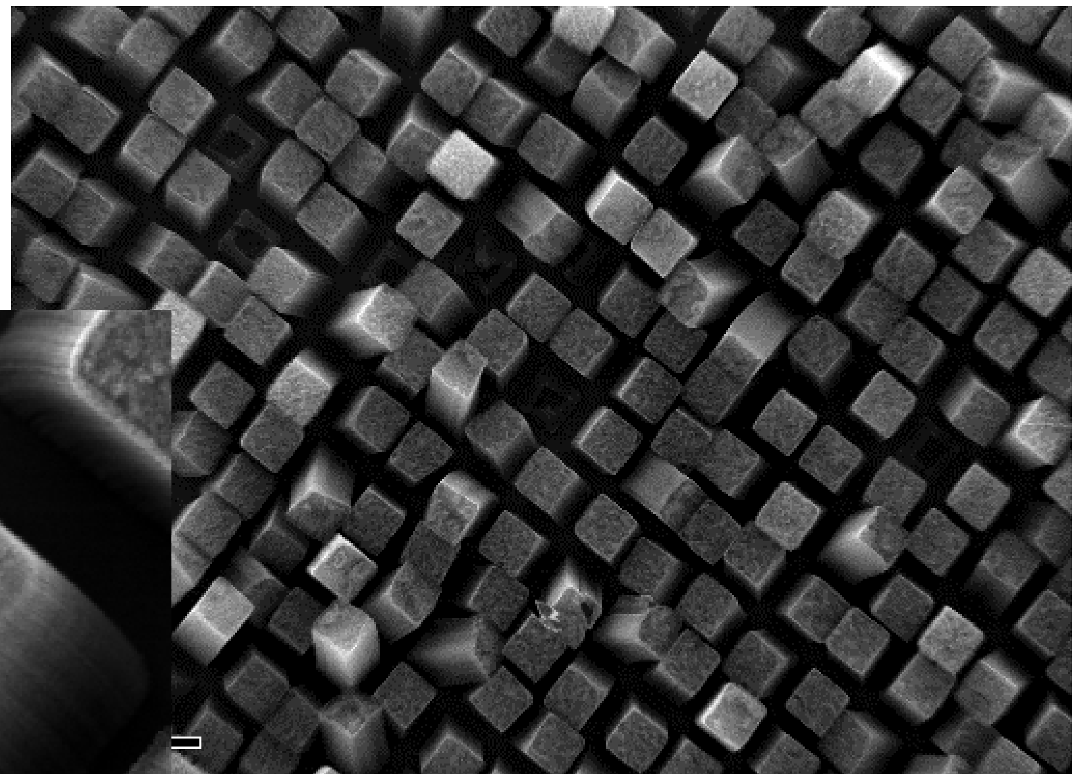
- 2 mw laser power, 1 μm focus spot
- Characteristic narrow band at 1590 cm^{-1}
- Signature band at 1730 cm^{-1} at SWNTs
- Diameter distribution 1.14 nm to 2 nm; consistent with TEM results
- High metallic % of NTs

Multiwall Nanotube Towers



- Surface masked by a 400 mesh TEM grid; 20 nm Al/ 10 nm Fe; nanotubes grown for 10 minutes



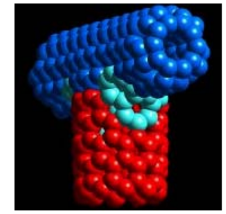


Grown using ethylene at 75

ICP Reactor for CNT Growth

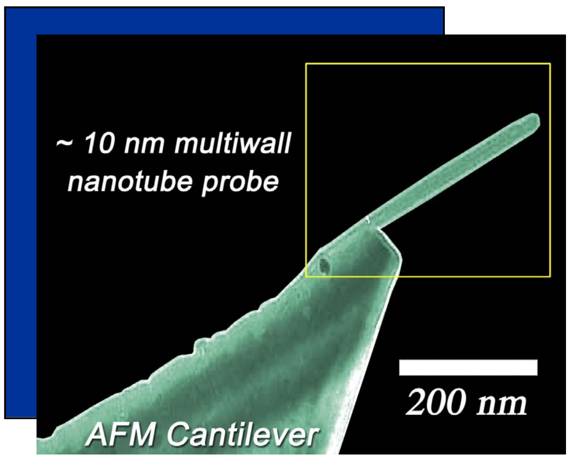
- Inductively coupled plasmas are the simplest type of plasmas; very efficient in sustaining the plasma; reactor easy to build and simple to operate
- Quartz chamber 10 cm in diameter with a window for sample introduction
- Inductive coil on the upper electrode
- 13.56 MHz independent capacitive power on the bottom electrode
- Heating stage for the bottom electrode
- Operating conditions
  CH_4/H_2 : 5 - 20%
  Total flow : 100 sccm
  Pressure : 1 - 20 Torr
  Inductive power : 100-200 W
  Bottom electrode power : 0 - 100 W

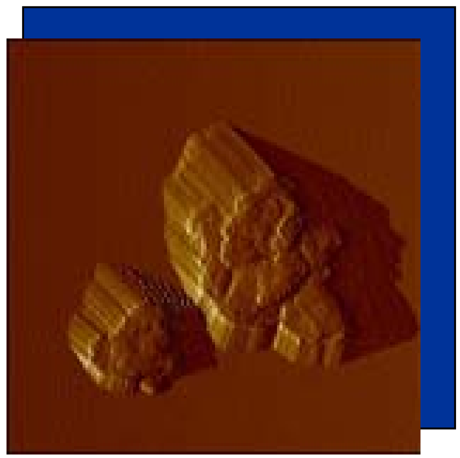
CNT in Microscopy



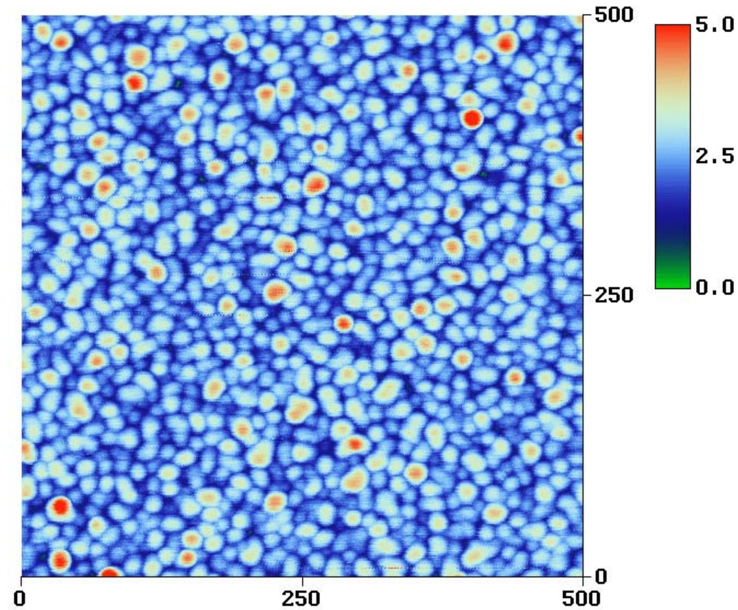
Atomic Force Microscopy is a powerful technique for imaging, nanomanipulation, as platform for sensor work, nanolithography...

Conventional silicon or tungsten tips wear out quickly. CNT tip is robust, offers amazing resolution.





Simulated Mars dust



2 nm thick Au on Mica

NASA Ames Research Center
Ramsey Stevens, Lance Delzeit, Cattien Nguyen

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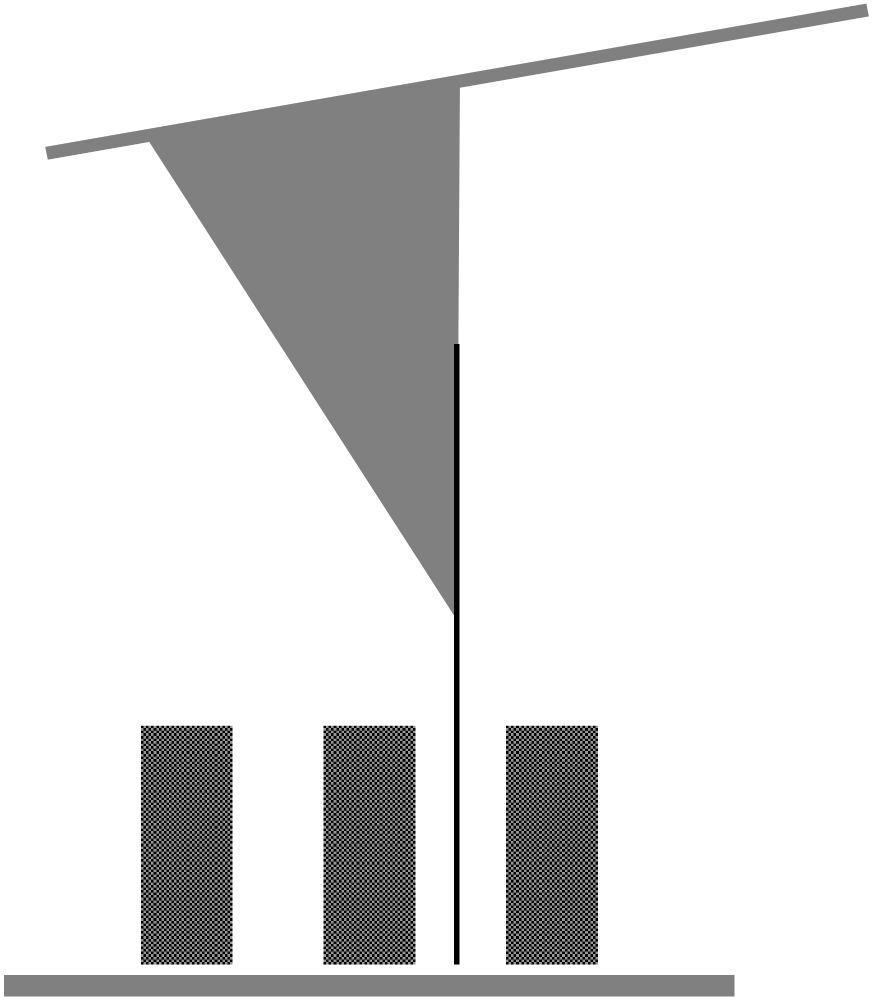
MWNT Scanning Probe



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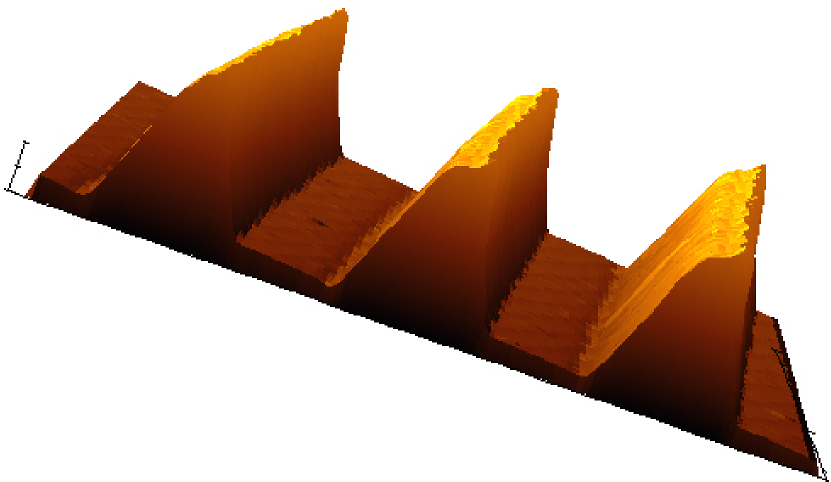
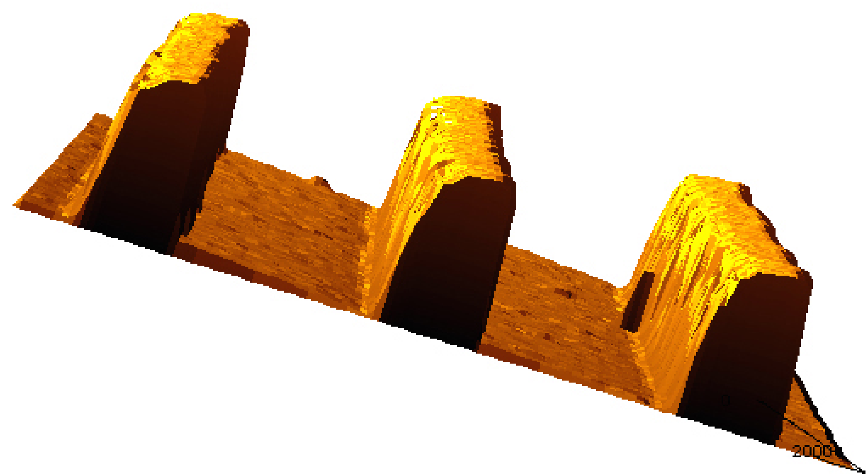
Profilometry in Integrated Circuit Manufacturing

280 nm line/space. Array of polymeric resist on a silicon substrate.



Conventional Si Pyramidal Cantilever



MWNT Probe

Nguyen et al., Nanotechnology, 12, 363 (2001).

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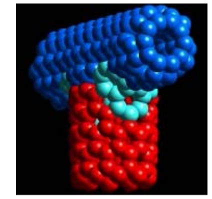
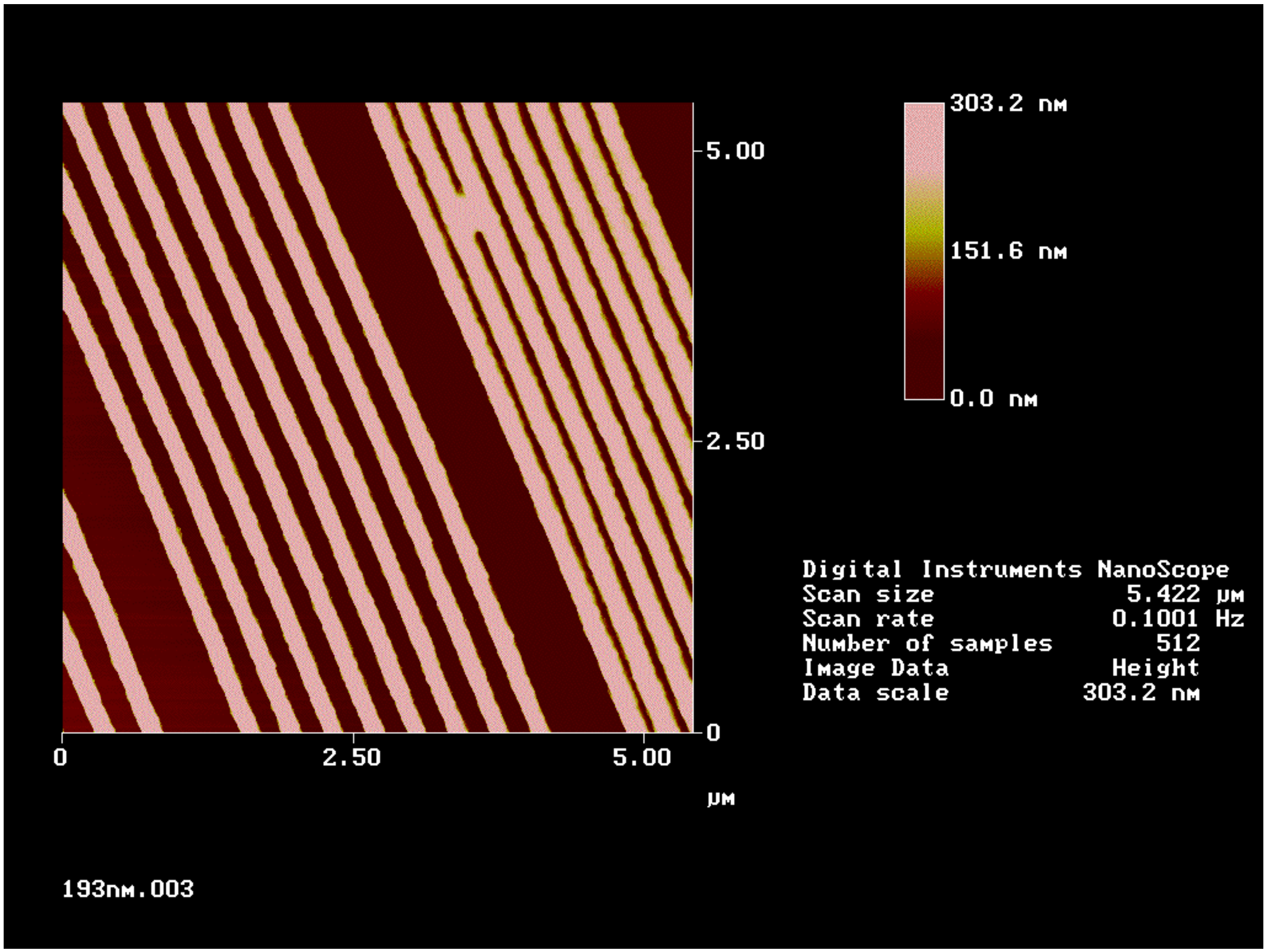
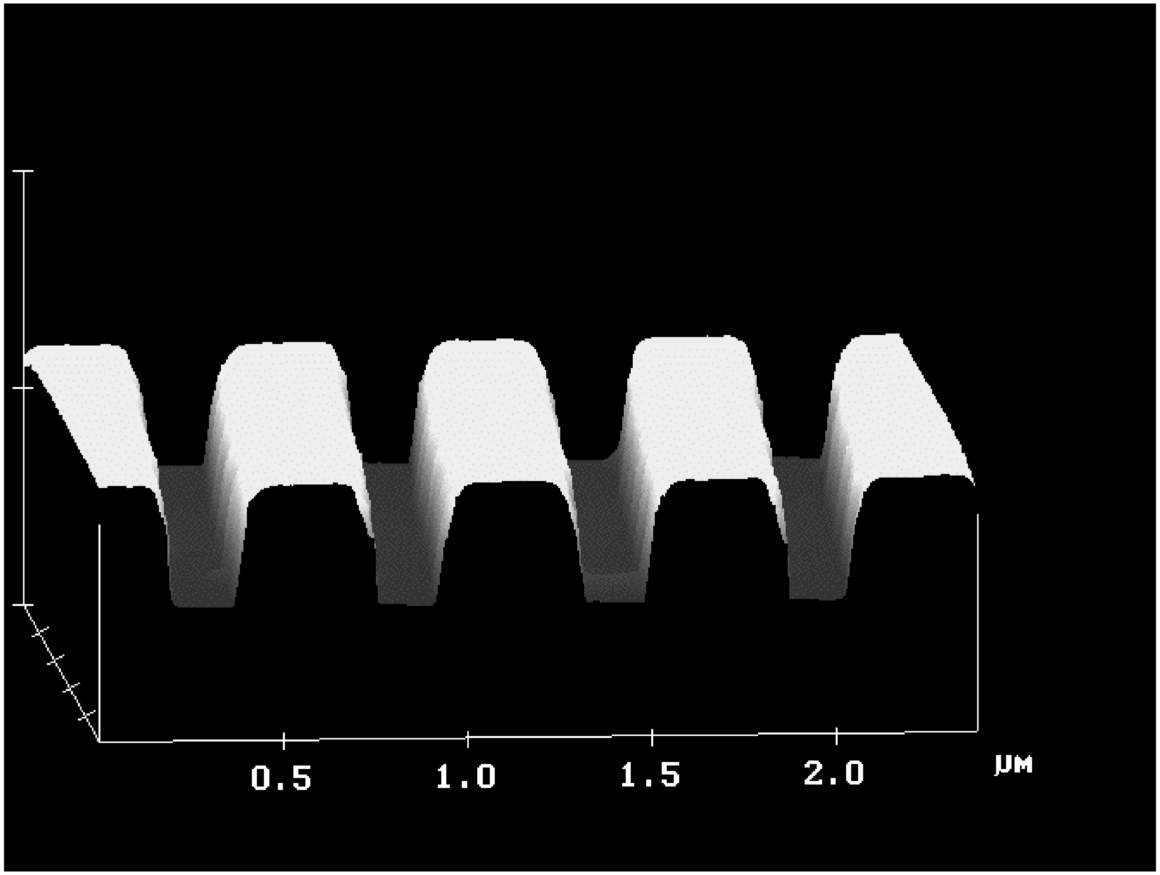
AFM Image with a MWNT Tip
193 nm IBM Version 2 Resist





AFM Image with MWNT Tip

DUV Photoresist Patterns Generated by Interferometric Lithography

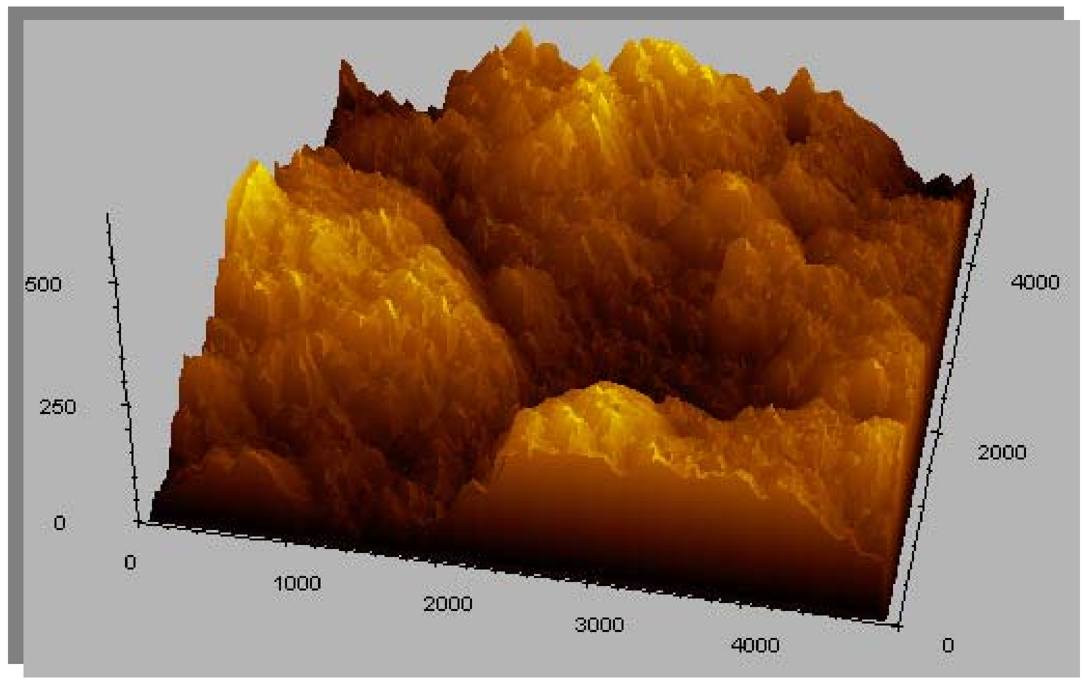


Nguyen et al., App. Phys. Lett., 81, 5, p. 901 (2002).

Imaging of Mars Analogs

Red Dune Sand (Mars Analog)

Optical image



AFM image using
carbon nanotube tip

High Resolution Imaging of Biological Materials

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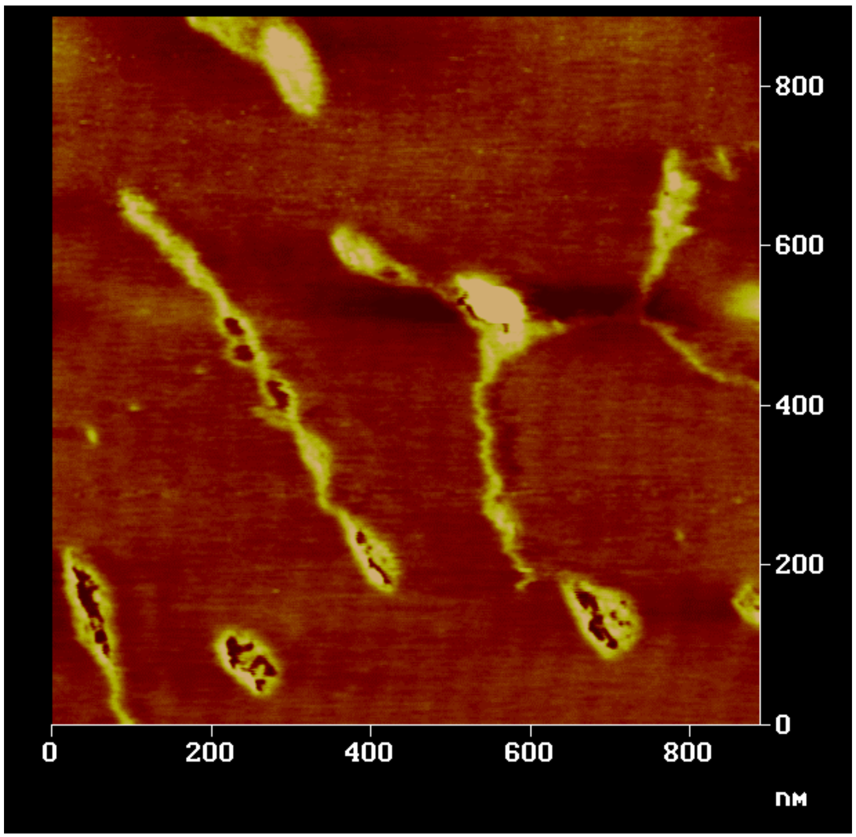
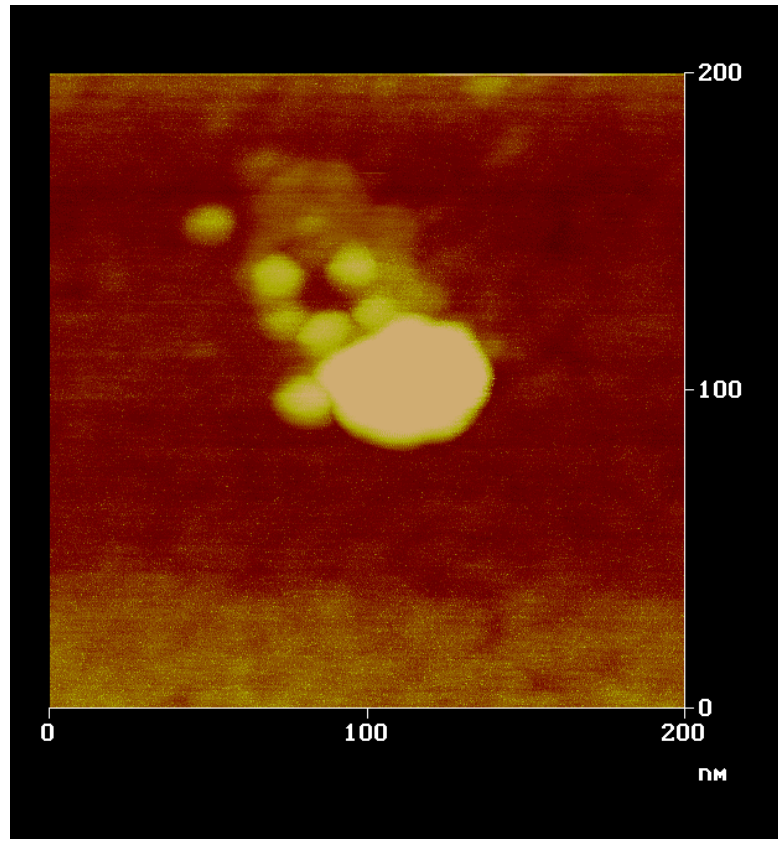


DNA



PROTEIN

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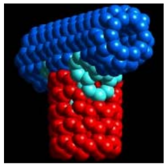
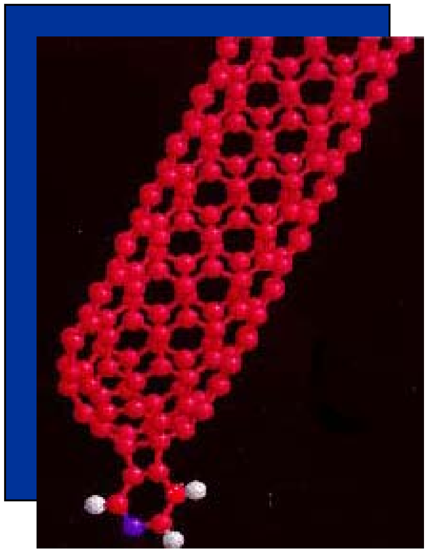
CNT Based Biosensors

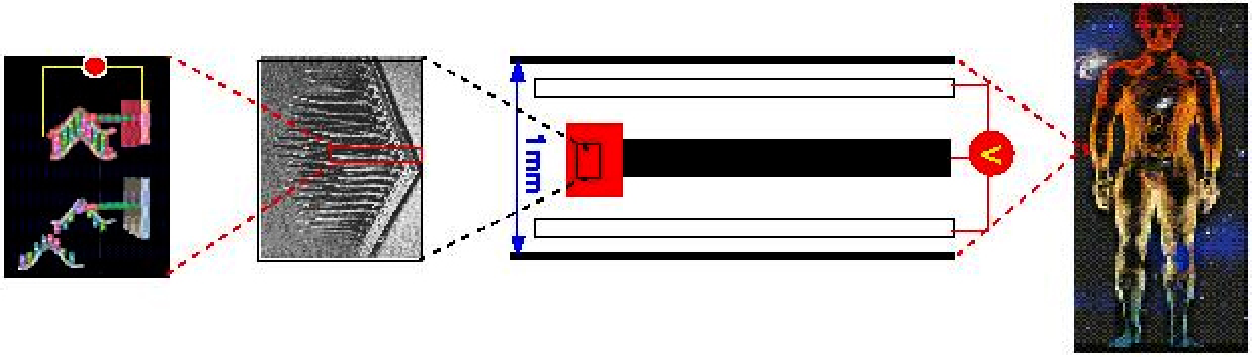


- Our interest is to develop sensors for astrobiology to study origins of life. CNT, though inert, can be functionalized at the tip with a probe molecule. Current study uses AFM as an experimental platform.

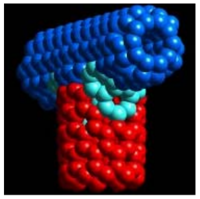


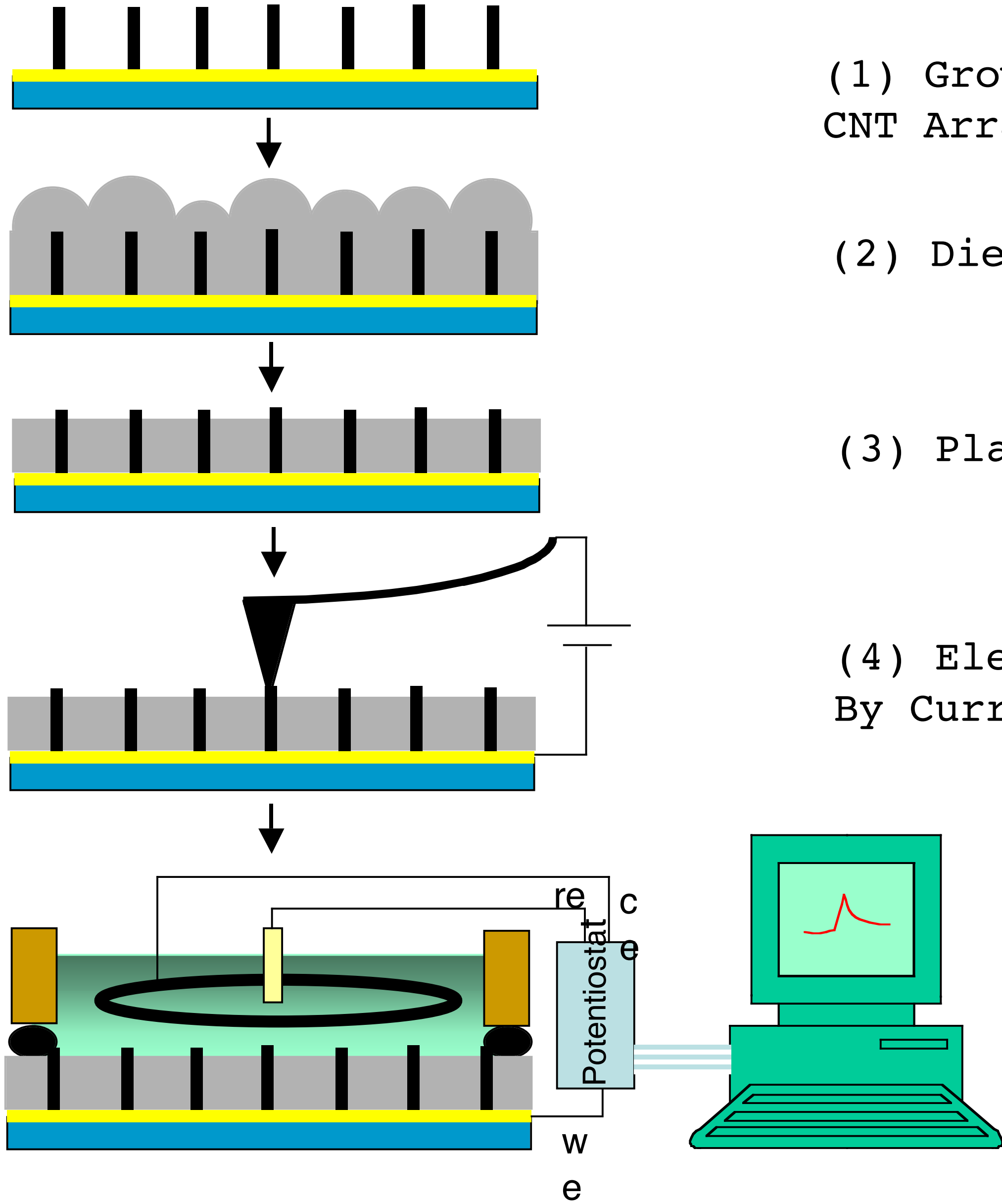
- The technology is also being used in collaboration with NCI to develop sensors for cancer diagnostics
  - Identified probe molecule that will serve as signature of leukemia cells, to be attached to CNT
  - Current flow due to hybridization will be through CNT electrode to an IC chip.
  - Prototype biosensors catheter development

High specificity
Direct, fast response
High sensitivity
Single molecule and cell signal capture and detection



The Fabrication of CNT Nanoelectrode Array





(1) Growth of Vertically Aligned CNT Array

(2) Dielectric Encapsulation

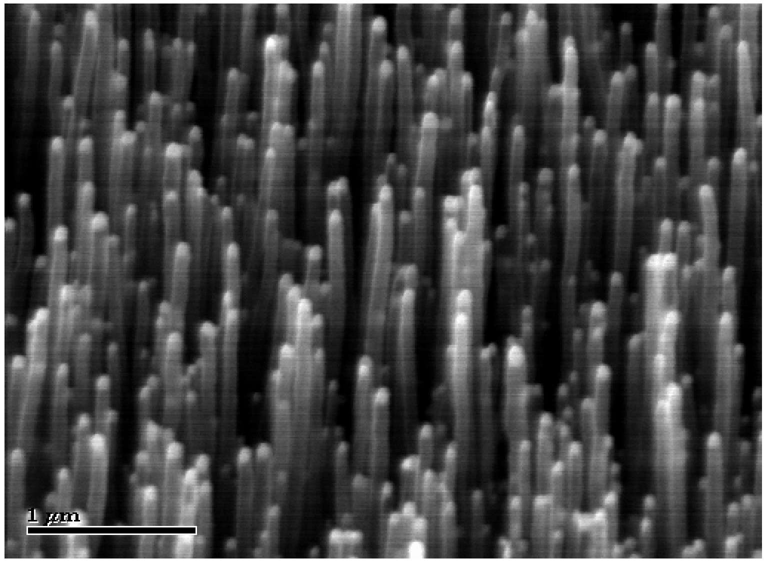
(3) Planarization

(4) Electrical Property Characteri
By Current-sensing AFM

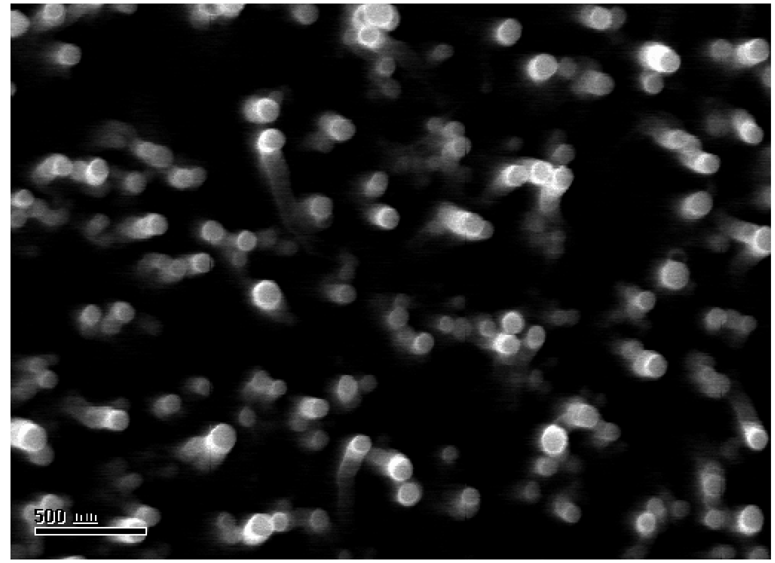
(5) Electrochemical Characterization

Fabrication of CNT Nanoelectrodes

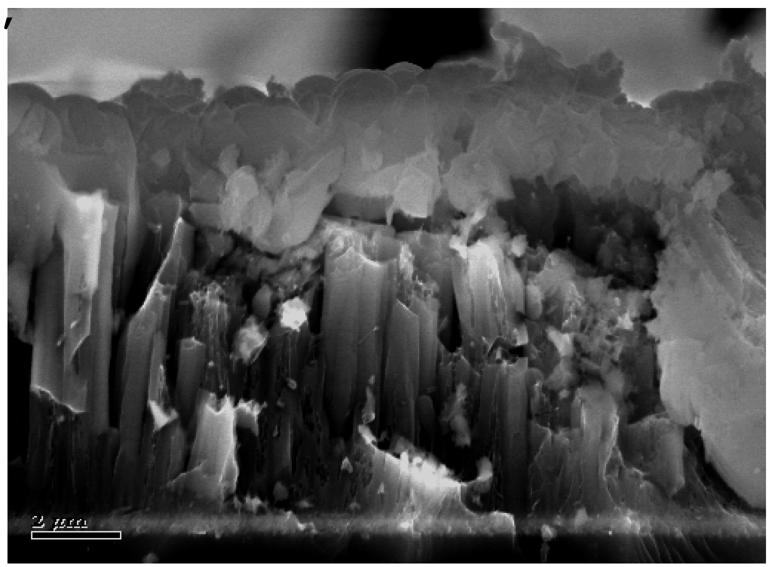
J. Li et al., Appl. Phys. Lett. 81 (5), 910 (2002)



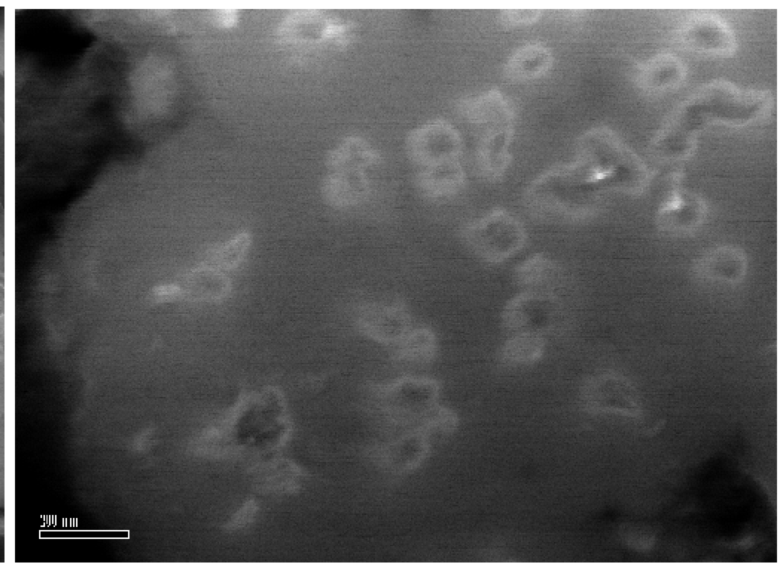
45 degree perspective view



Top view

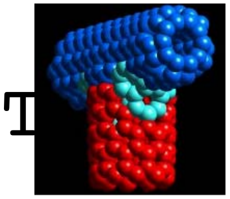


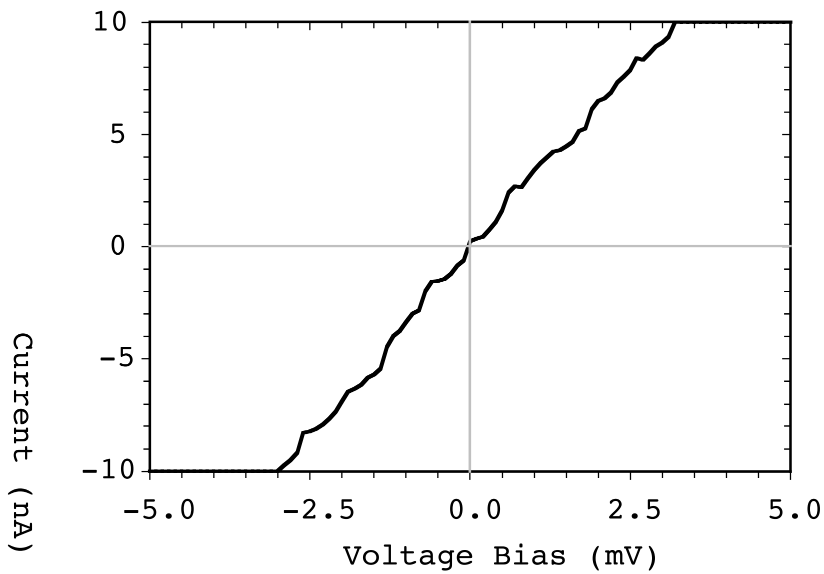
Side view after encapsulation

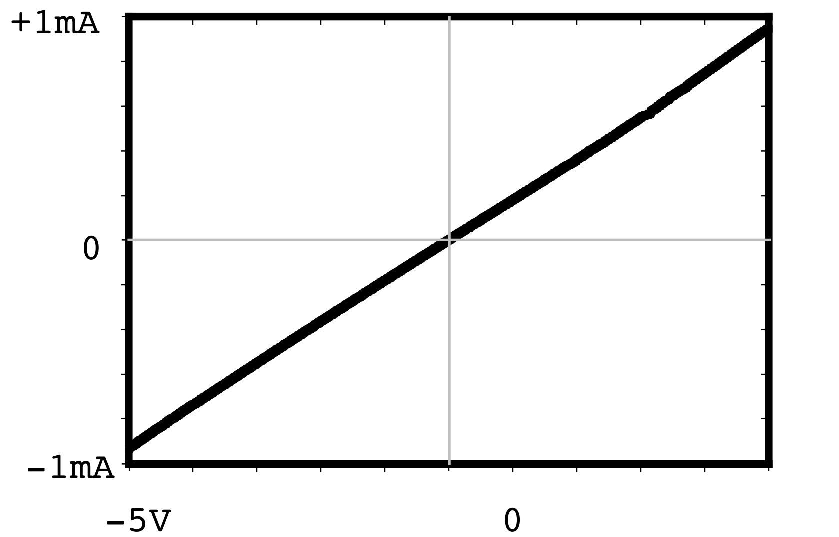


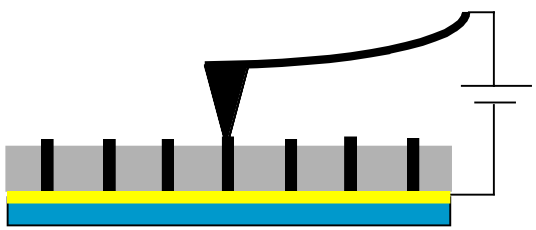
Top view after planarization

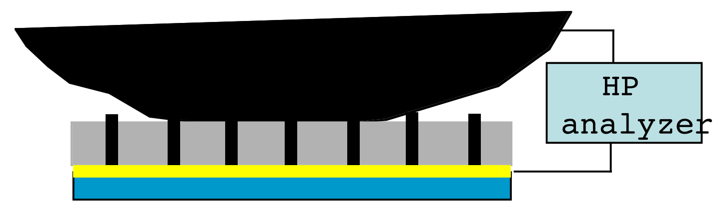
Electrical Properties of CNT







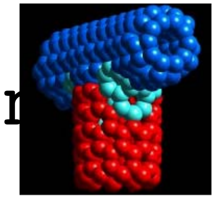


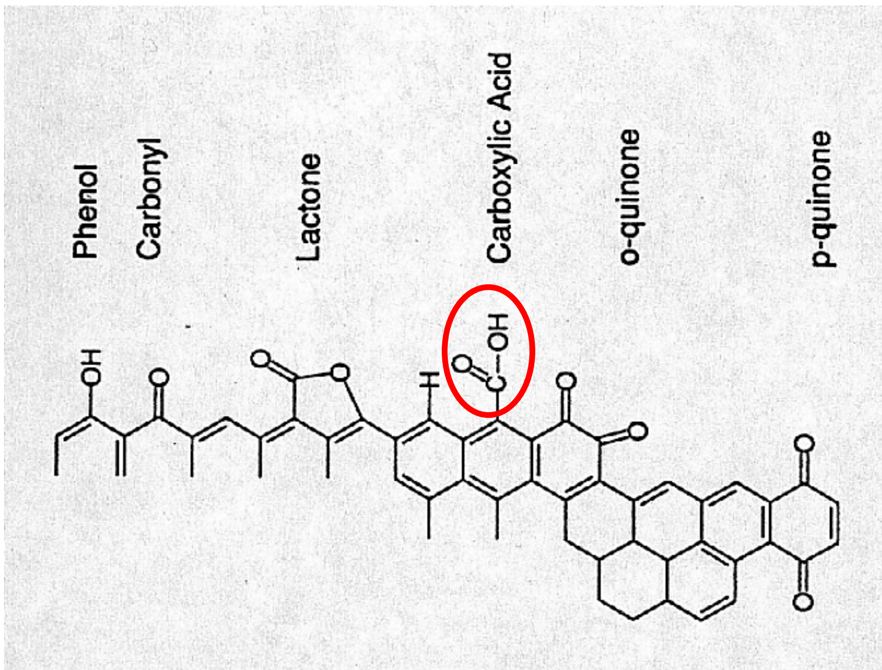


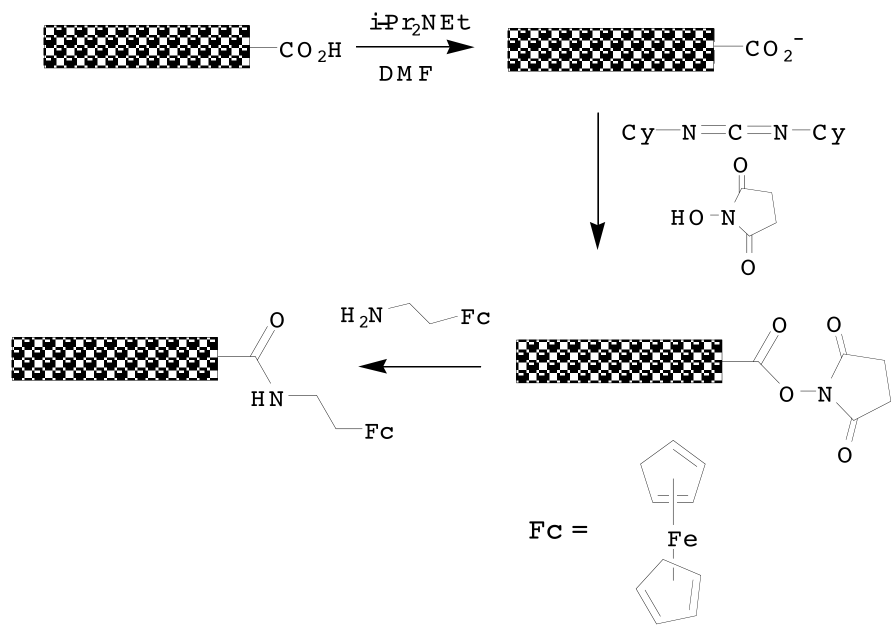
Current Sensing AFM

Four-probe station
And HP parameter analyzer

Chemical Functionalization

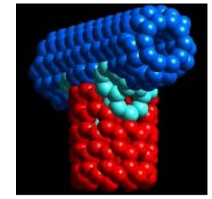


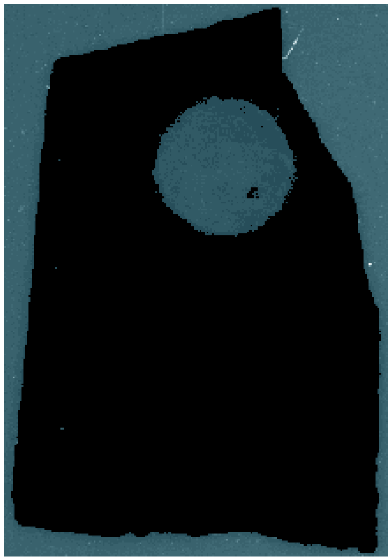




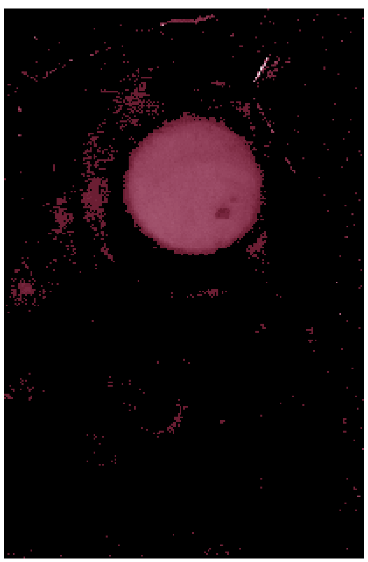
Highly selective reaction of primary amine with surface –COOH group

Functionalization of DNA

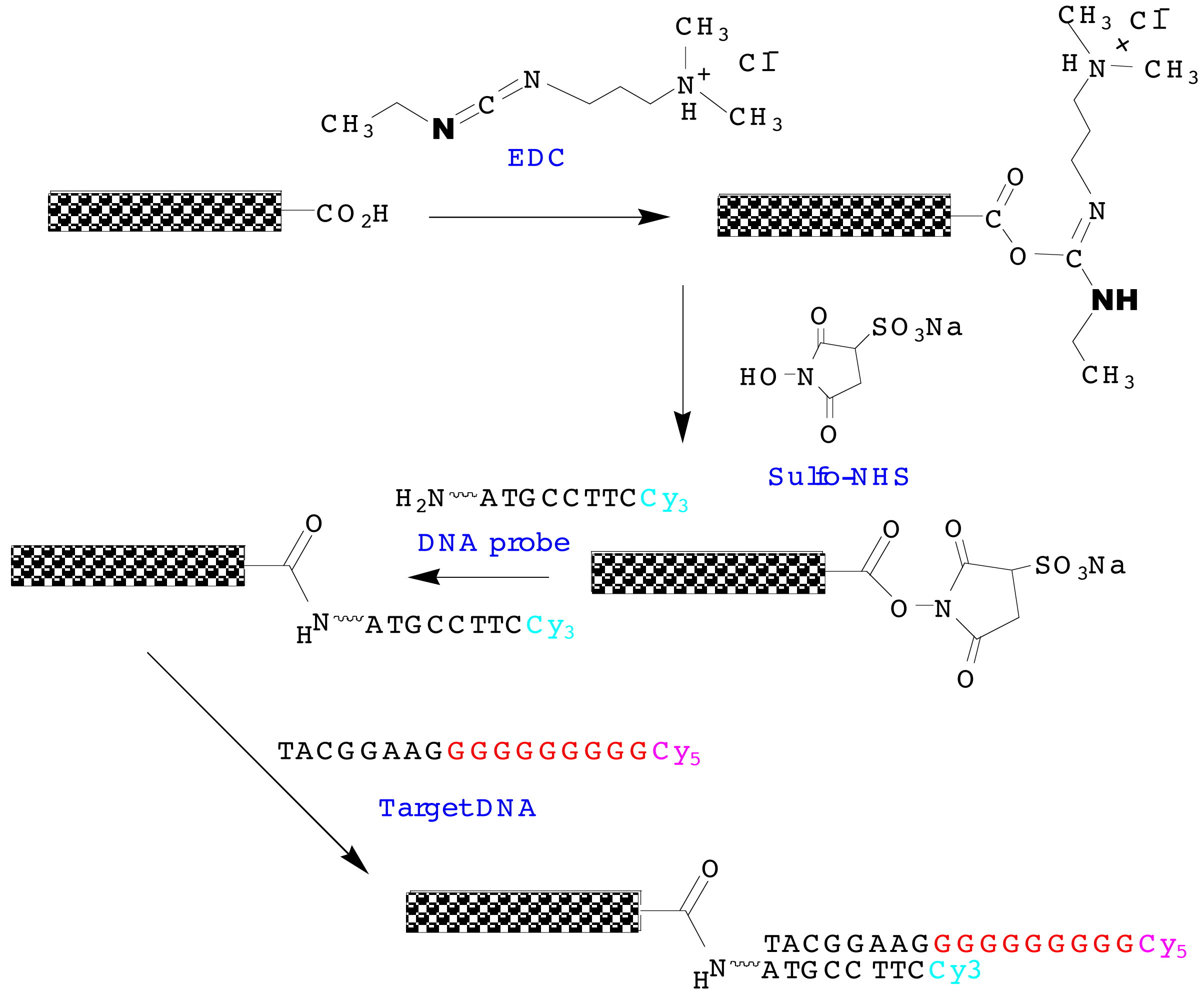




Cy3 image



Cy5 image



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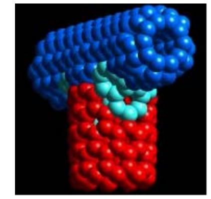
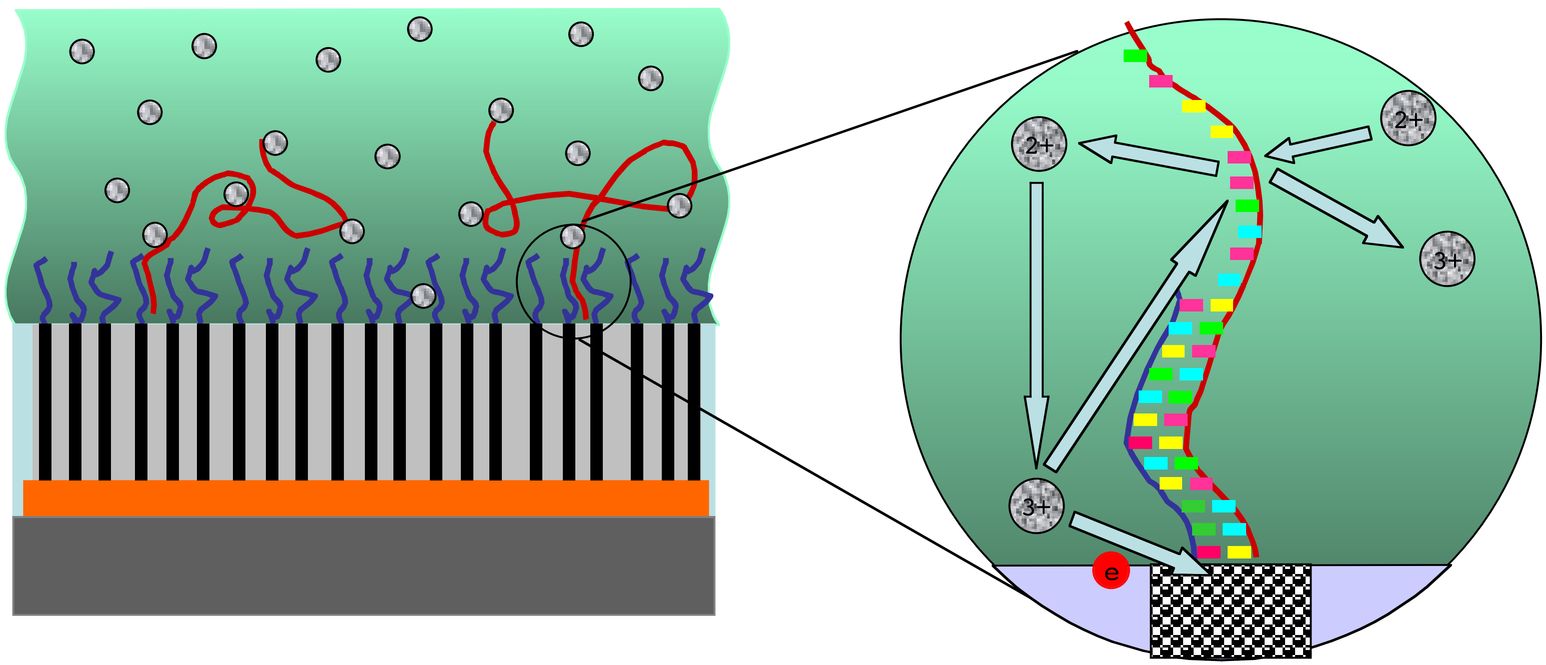


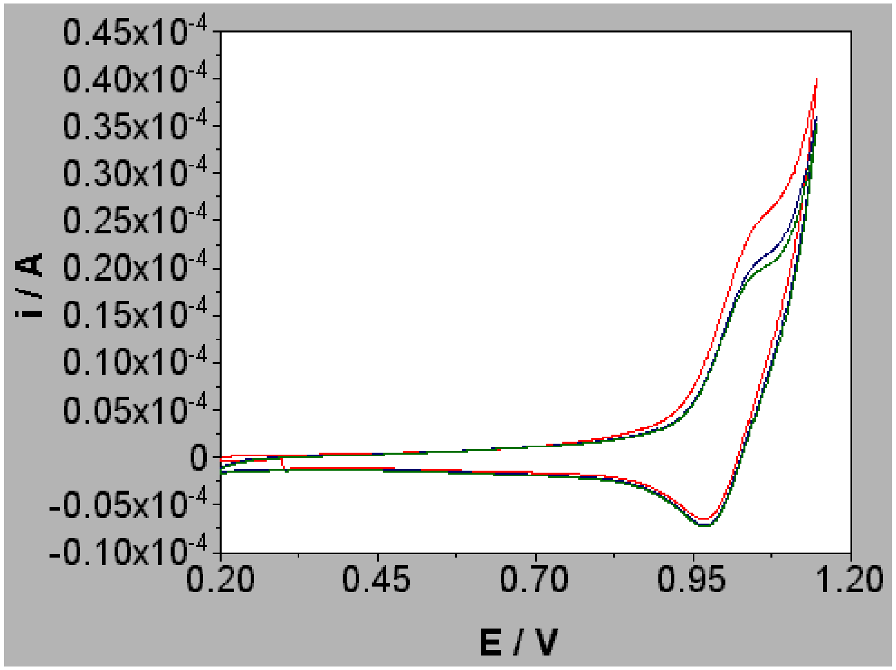
CNT DNA Sensor Using Electrochemical Detection

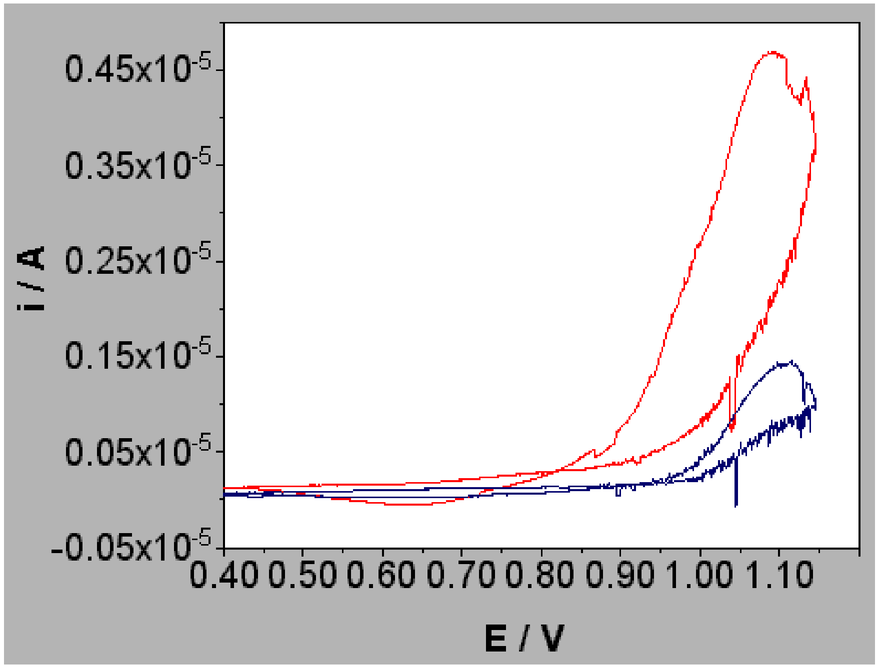


- **MWNT array electrode functionalized with DNA/PNA probe as an ultrasensitive sensor for detecting the hybridization of target DNA/RNA from the sample.**
  - Signal from redox bases in the excess DNA single strands

- **The signal can be amplified with metal ion mediator** $\left[Ru(bPy)_3^{2+}\right]$ **oxidation catalyzed by Guanine.**

Electrochemical Detection of DNA Hybridization



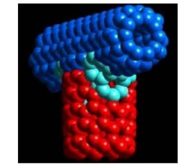


1st, 2nd, and 3rd cycle in cyclic voltammetry

1st – 2nd scan: mainly DNA signal

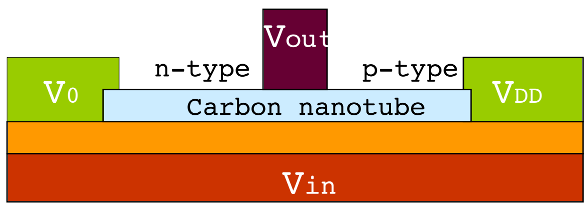
2nd – 3rd scan: Background

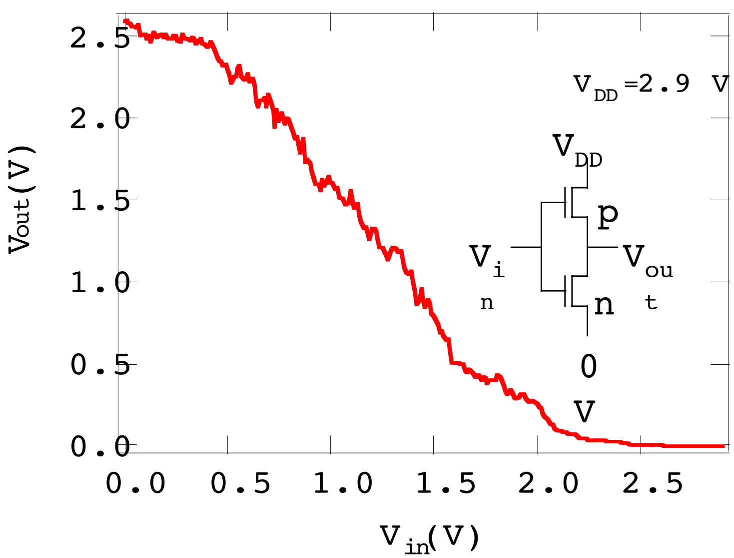
CNT-based Logic and Memory Devices

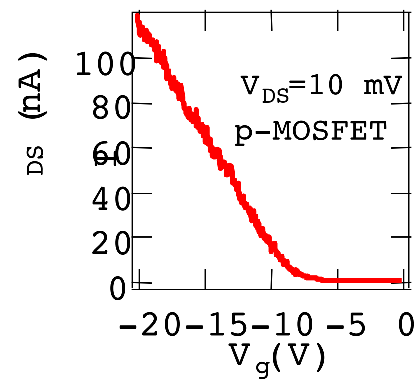


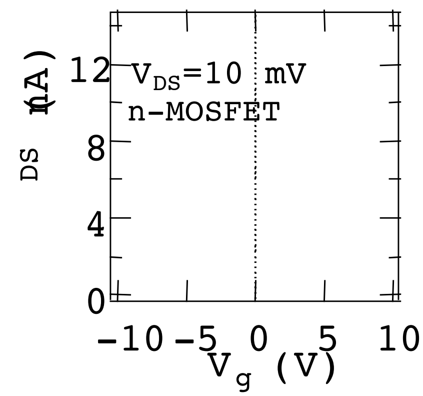
*First single nanotube logic device demonstration: Inverter (Appl. Phys. Lett., Nov. 200

by Chongwu Zhou (USC) and Jie Han (NASA Ames)

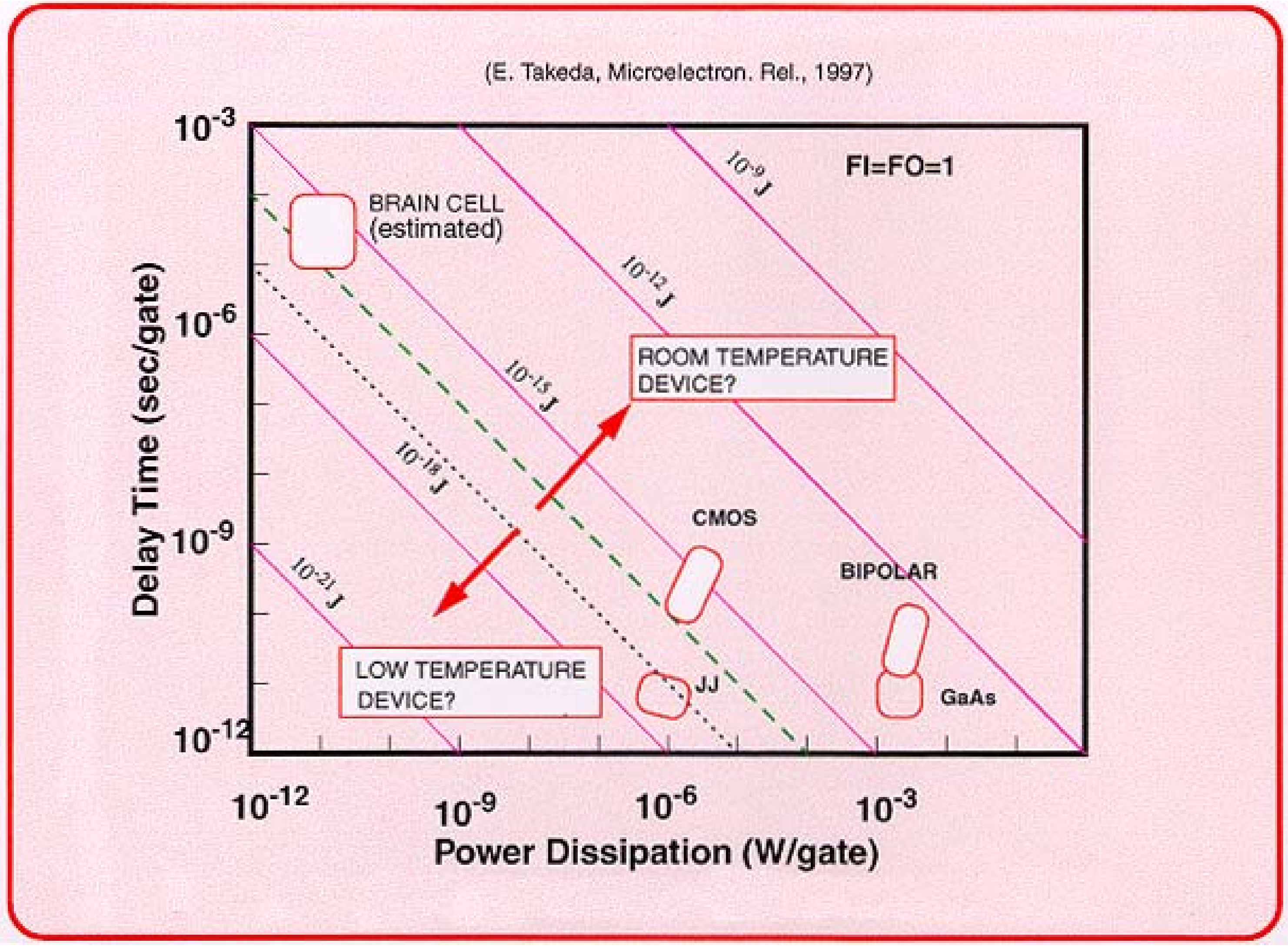






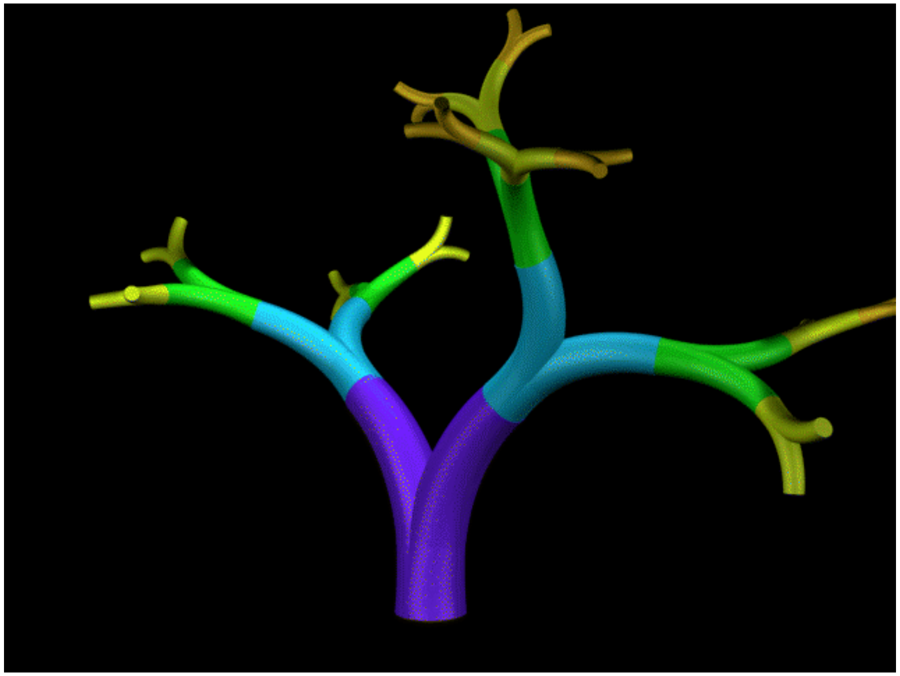


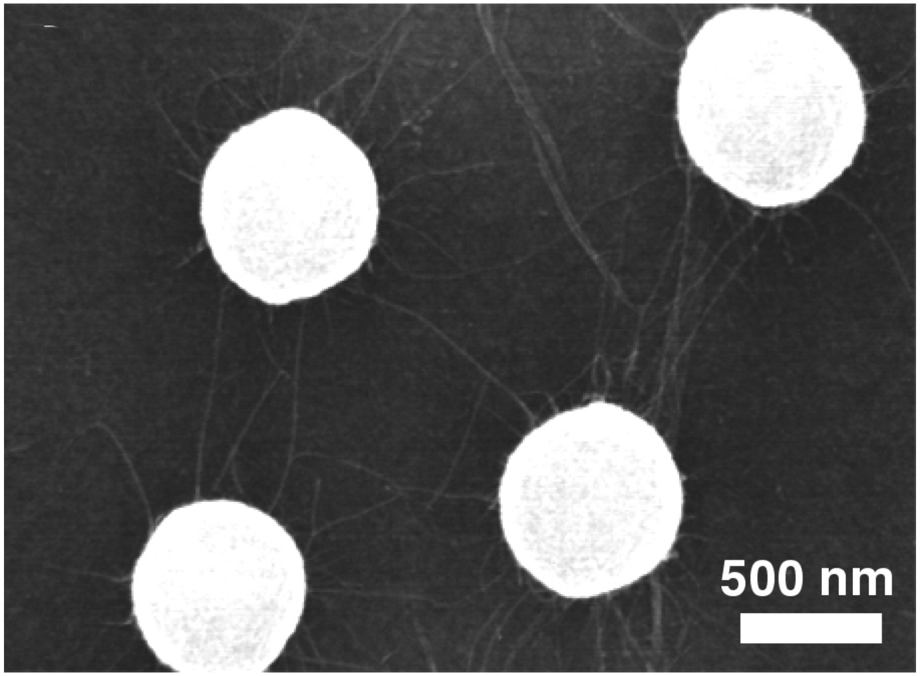
Switching Energy of Electron Devices and Brain Cells



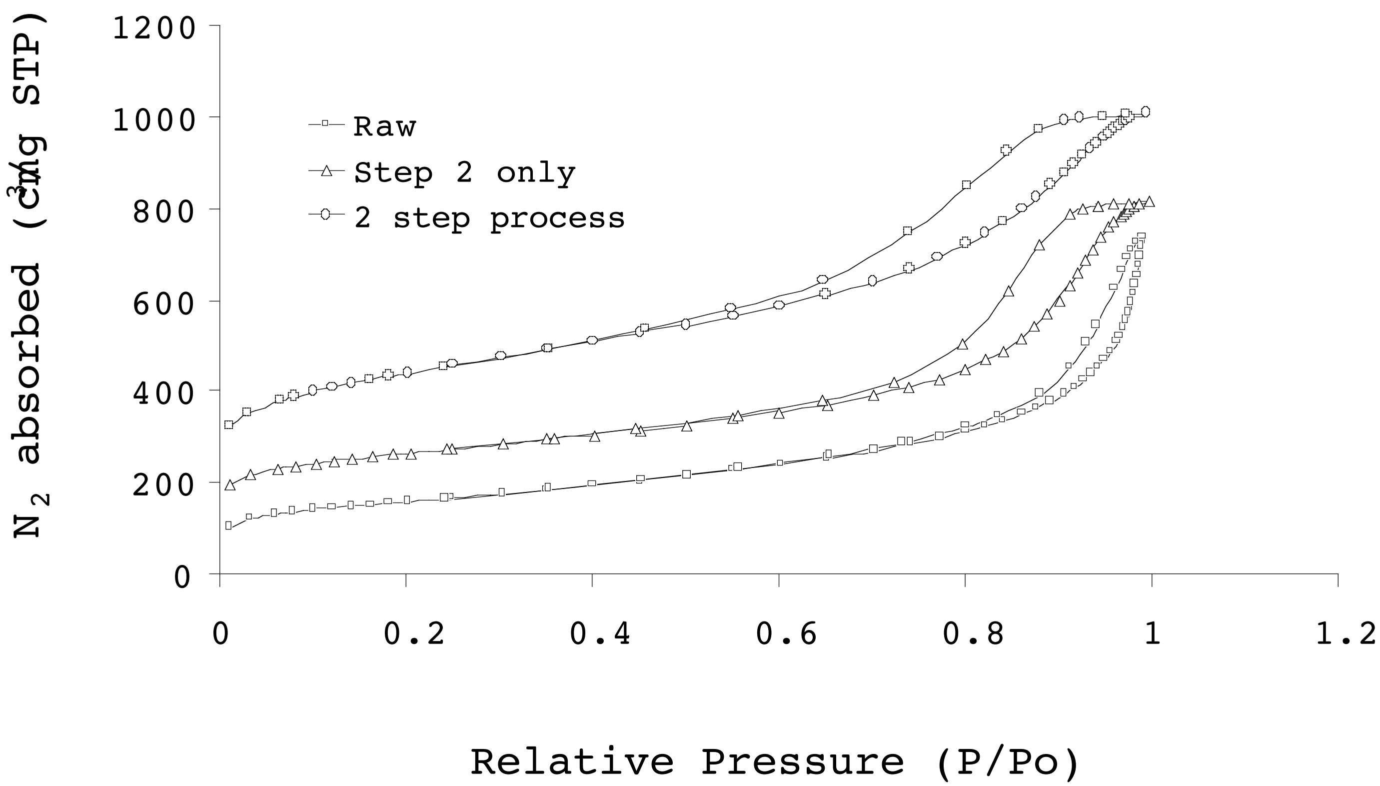
Four-level CNT Dentritic Neural Tree

- Neural tree with 14 symmetric Y-junctions
- Branching and switching of signals at each junction similar to what happens in biological neural network
- Neural tree can be trained to perform complex switching and computing functions
- Not restricted to only electronic signals; possible to use acoustic, chemical or thermal signals



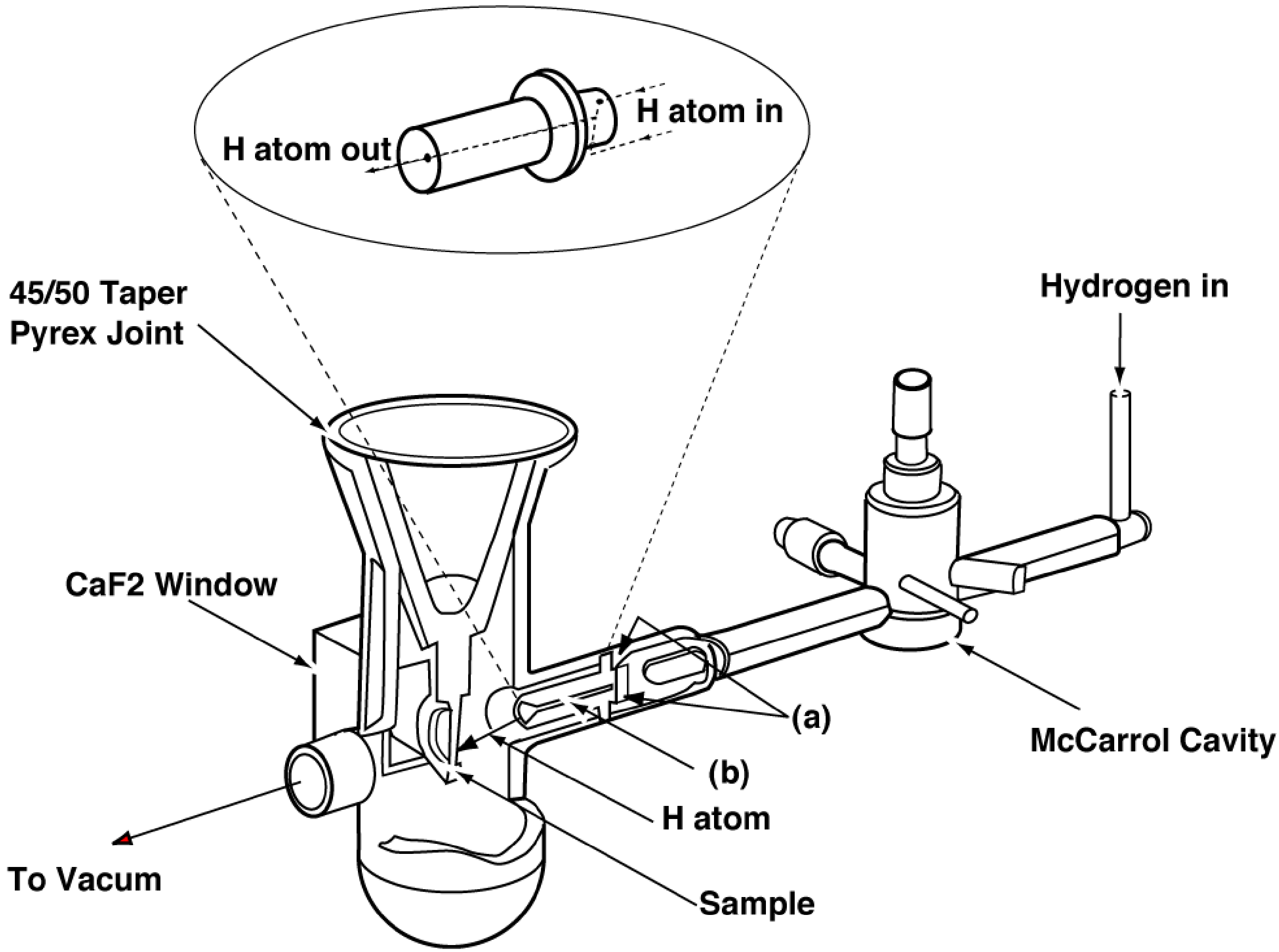


N_2 Adsorption Isotherm

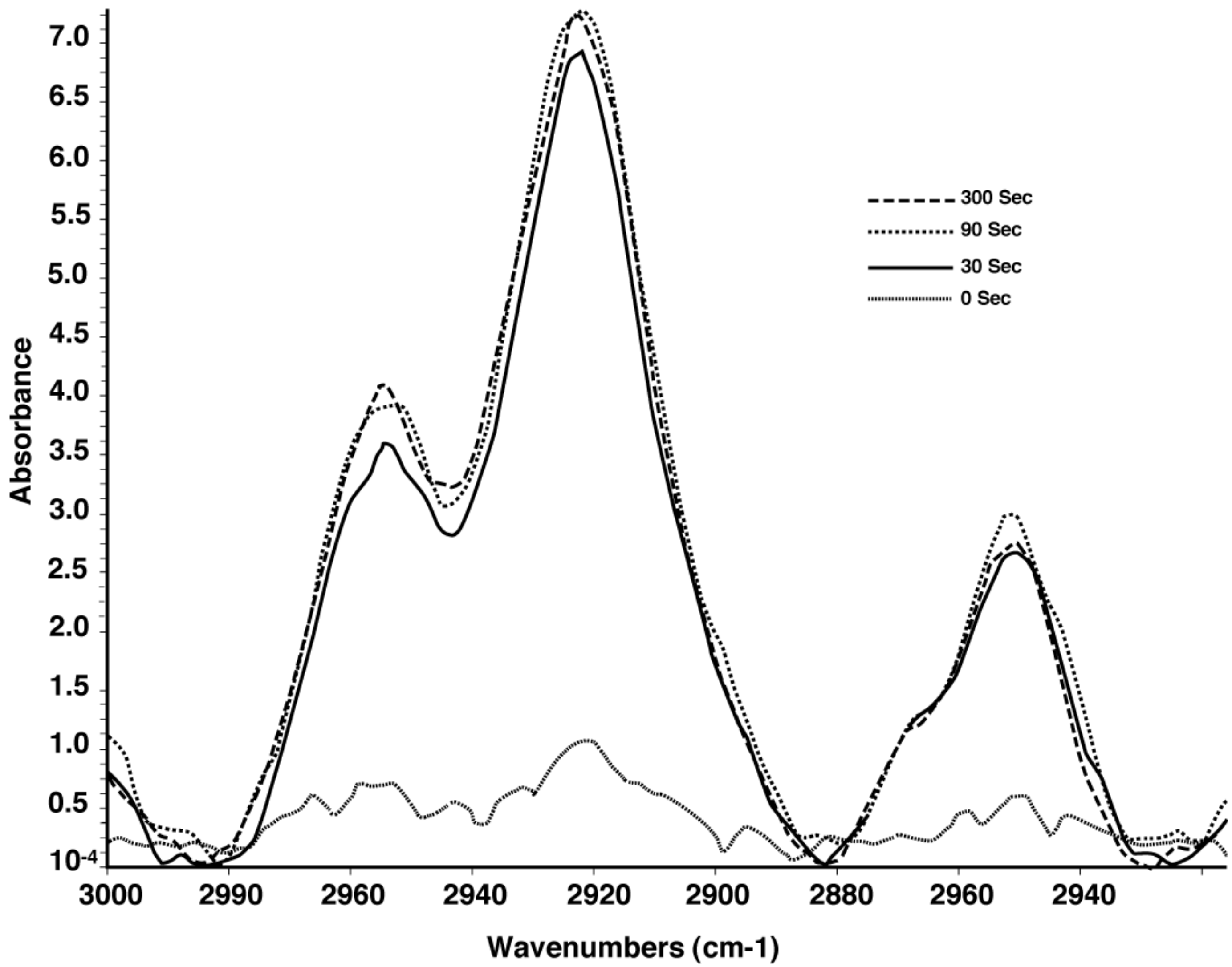


- Estimated surface area of purified HiPCo SWNTs is 1580 m^2/gm
- Applications in catalysis, gas absorption….

Functionalization Using a Glow Discharge



Atomic H Functionalization: FTIR



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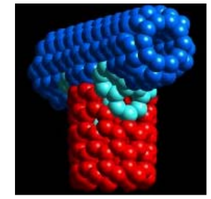
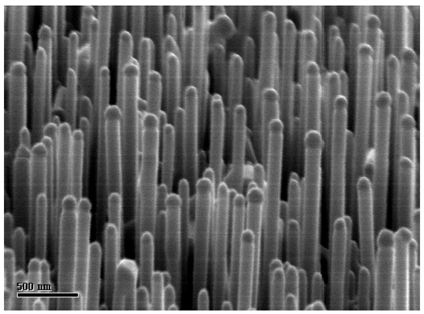
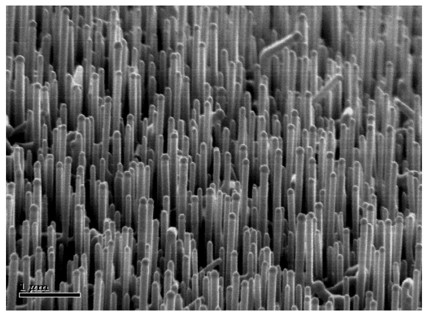
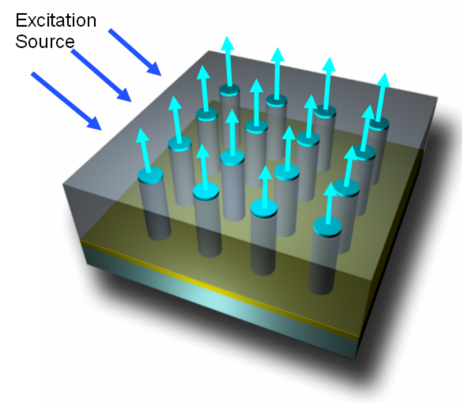
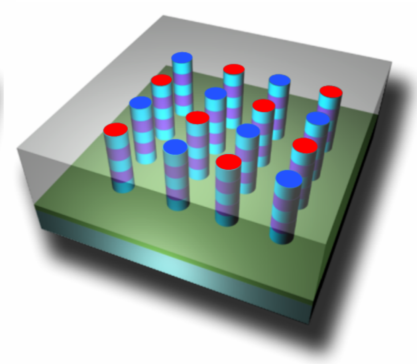
Zinc Oxide Nanowires

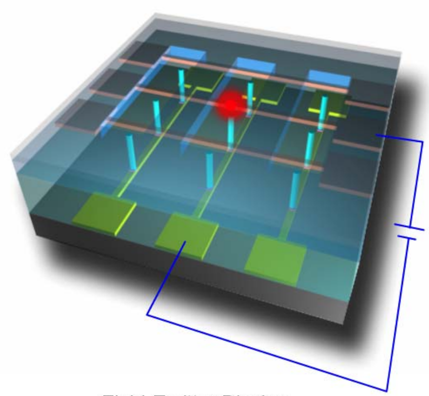




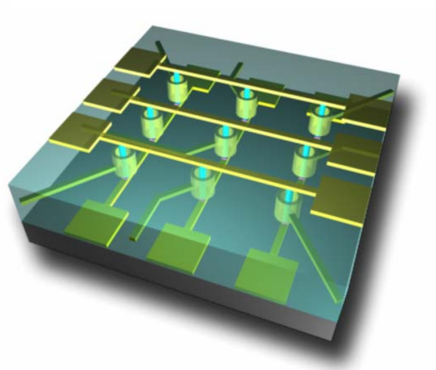




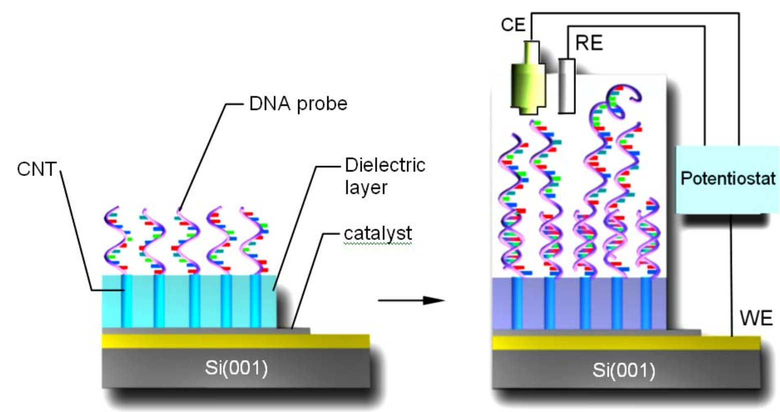




Field-Emitter Display



Vertical Transistor Arrays



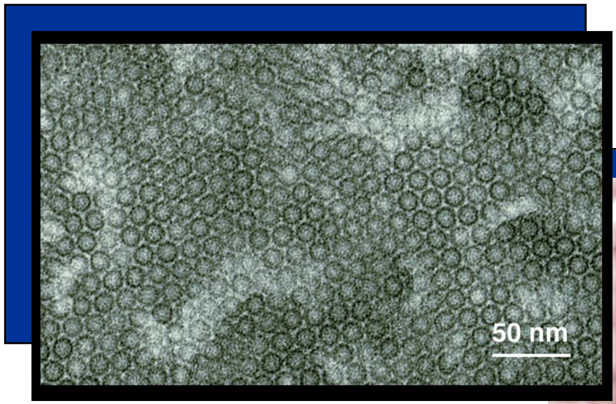
Functionalization

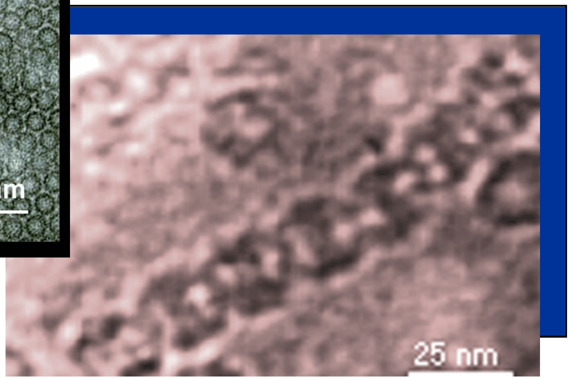
Detection

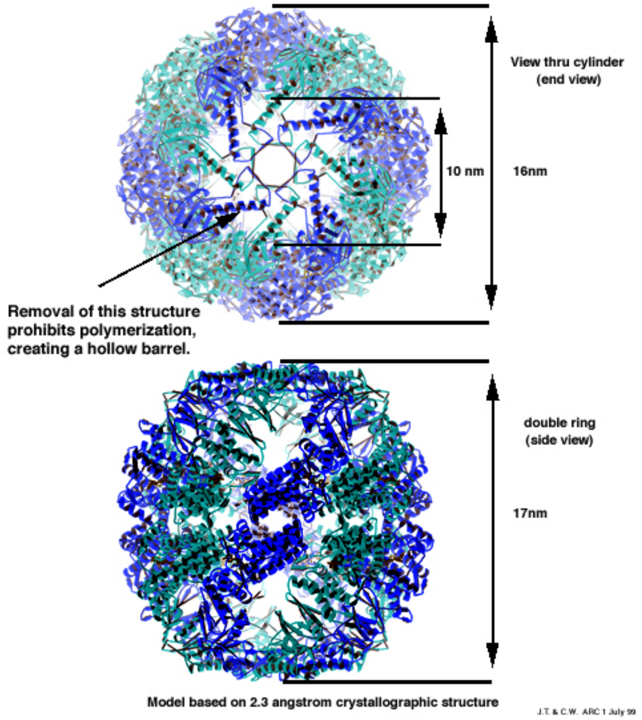
Protein Nanotubes

- Heat shock protein (HSP 60) in organisms living at high temperatures ("extremophiles") is of interest in astrobiology

- HSP 60 can be purified from cells as a double-ring structure consisting of 16-18 subunits. The double rings can be induced to self-assemble into nanotubes.







Extremophile Proteins for Nano-scale Substrate Patterning

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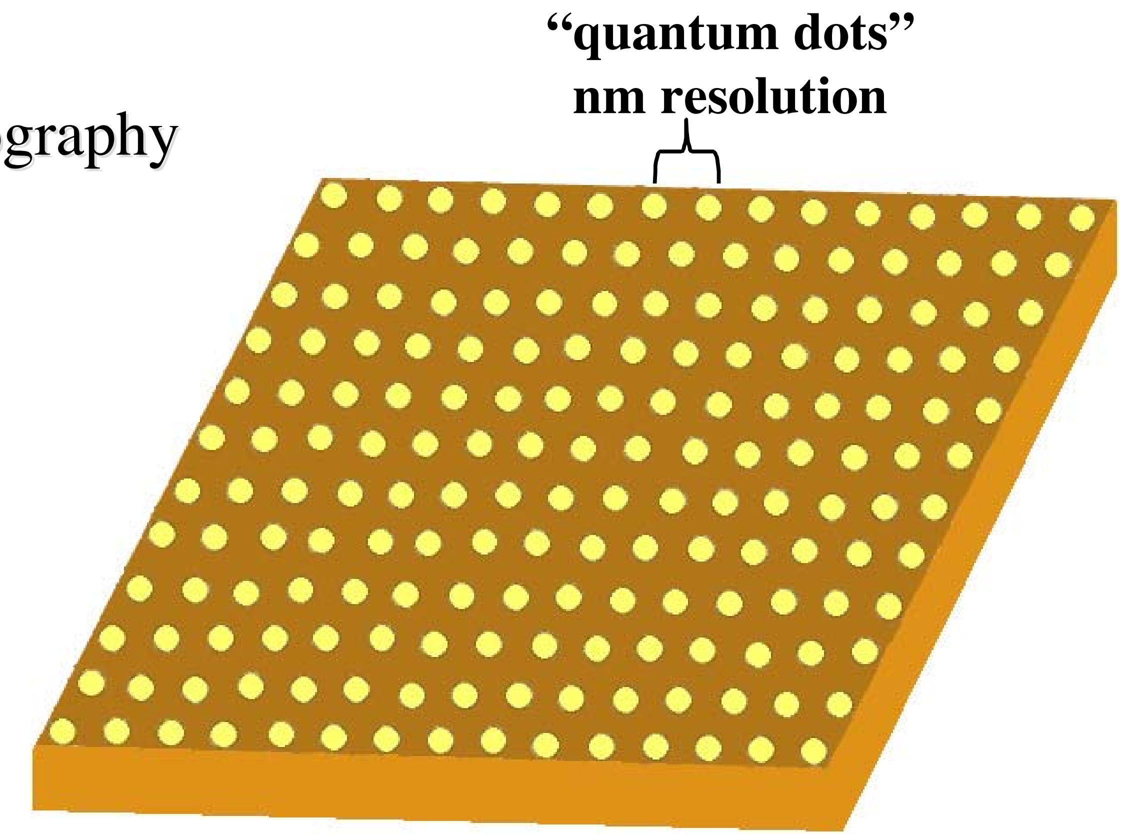
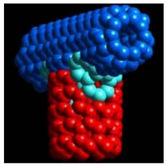
Nano-scale engineering for high resolution lithography

Future: Bio-based lithography
- Batch self-assembly
- Evolving
- Inexpensive

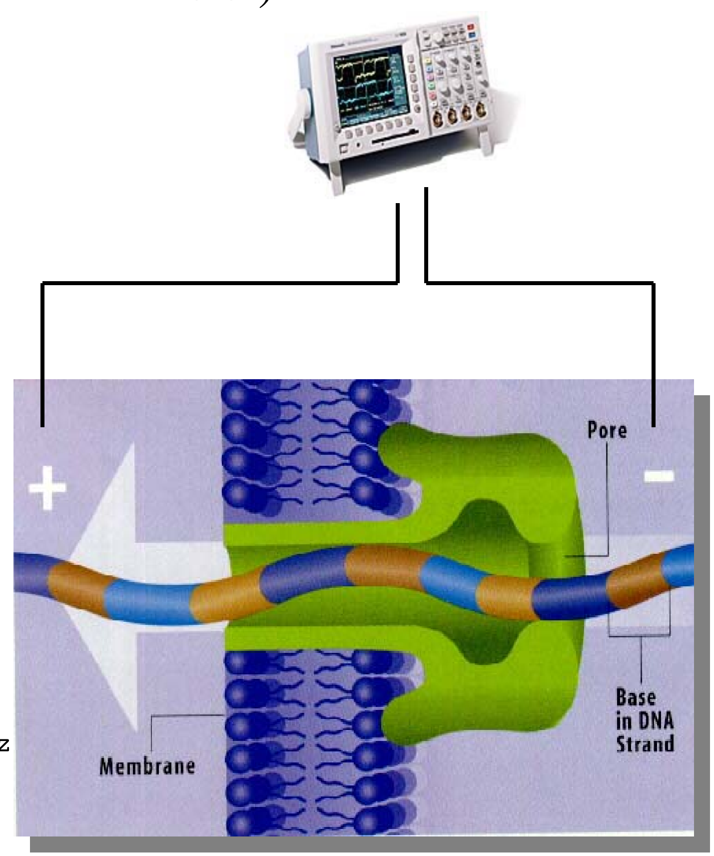


DNA Sequencing with Nanopores

The Concept

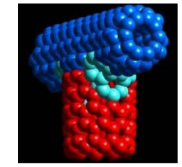


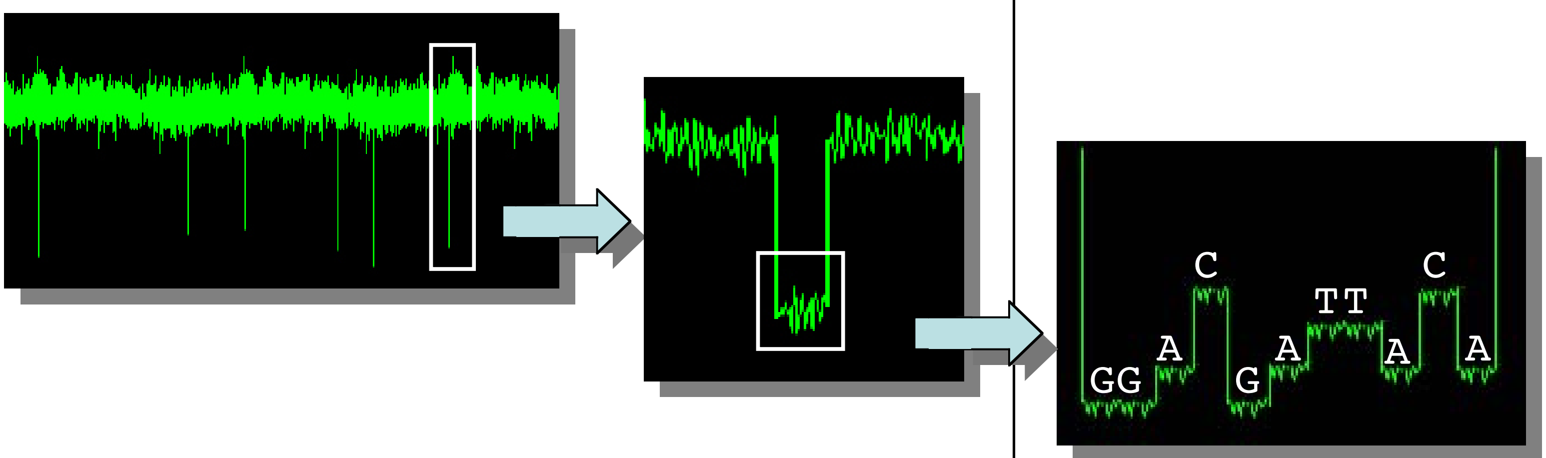
- Nanopore in membrane (~2nm diameter)
- DNA in buffer
- Voltage clamp
- Measure current



G. Church, D. Branton, J. Golovchenko, Harvard
D.Deamer, UC Santa Cruz

The Sequencing Concept

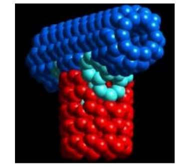




Present

Future

Summary



- Nanotechnology is an enabling technology that will impact electronics and computing, materials and manufacturing, energy, transportation….

- The field is interdisciplinary but everything starts with material science. Challenges include:
  - Novel synthesis techniques
  - Characterization of nanoscale properties
  - Large scale production of materials
  - Application development

- Opportunities and rewards are great and hence, tremendous worldwide interest

- Integration of this emerging field into engineering and science curriculum is important to prepare the future generation of scientists and engineers